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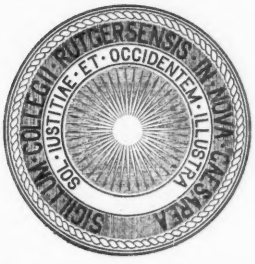

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SOIL SCIENCE

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ON THE USE OF THE CONVENTIONAL CARBON FACTOR IN ESTIMATING SOIL ORGANIC MATTER

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Arkansas Agricultural Experiment Station

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Since the researches of Schulze, Wolff, Fresenius, and van Bemmelen, the use of the conventional carbon factor to estimate the organic matter in soils has been in general practice. The question has been raised at various times regarding the justification of this method for the determination of soil organic matter, and the object of this paper is to present more conclusive data on the problem. The following references include the more important studies in this field:

Schulze (6, p. 258) claims that 58 parts of carbon on an average represent 100 parts of organic matter in soil, and 60 parts represent 100 parts of humus.

Wolff (9) assumes that the percentage of carbon in "humus" is 58, and determines the organic matter of the soil by multiplying the organic carbon by the factor 1.724 or the carbon dioxide by 0.471.

Van Bemmelen (7) multiplies the amount of organic carbon by the factor 1.724 in order to obtain the organic matter in a soil.

Warington and Peake (8) give their results with three methods for the determination of organic carbon in soil. They find the relation of carbon to be fairly constant, the average being 79.9 per cent of carbon found by oxidation with chromic acid, 92.4 per cent by oxidation with potassium permanganate, for 100 yielded by combustion in oxygen. They also compare the organic matter of the soils studied, as determined by loss on ignition, to the organic matter calculated from the carbon found by combustion in oxygen, assuming with Schulze, Wolff and Fresenius that carbon is 58 per cent of the organic matter. In all cases the loss on ignition is considerably in excess of the organic matter calculated from the carbon factor, even when the soil has been dried at 150°C. For this reason these investigators consider it necessary to determine directly the percentage of carbon in order to measure with any degree of accuracy the organic matter present.

Loges (3) refers to the general use of the carbon factor among the German experiment stations in estimating soil organic matter. A large number of soils was studied and experimental data are tabulated showing the wide difference existing between the results obtained by oxidation with chromic acid and those secured by ignition. The results of Loges corroborate those of Warington and Peake. The lower values by the chromic acid method are attributed to the formation of some acetic acid.

Cameron and Breazeale (1) report their investigations on the organic matter in soils and subsoils as determined by their modified chromic acid method for estimating the organic carbon. In 1900 these investigators discovered in 32 out of 84 cases that the loss on ignition method gave a higher percentage of organic matter in the subsoils than in the corresponding surface soils. Finding combustion in a tube slow and unsatisfactory an improved chromic acid method was adopted. They conclude from their results that "there is not sufficient ground as yet for advocating the use of any other factor than the usually accepted one for the calculation of the organic matter from the carbon dioxide obtained in the combustion," and recommend the conventional factor as established by Wolff, Van Bemmelen, and Wollny.

More recently Gortner (2) states that "Inasmuch as the 'humus' extract of soils is undoubtedly a mixture of organic compounds, many of which are colorless and in all probability are extracted from unchanged plant or animal materials, and inasmuch as the soil pigment present in this solution probably rarely exceeds 40 per cent of the humus, a determination of the humus as ordinarily carried out appears to be wholly without scientific justification. The European method of reporting 'humus,' by making a determination of total organic carbon, appears to be far preferable."

In the fall of 1919 we undertook a thorough investigation of the percentage of carbon in soil organic matter, employing the modified rapid dry combustion method (5) devised especially for this investigation, which has been reported elsewhere. One-gram samples of soil were prepared for the determination in accordance with the method described by Rather (4). Inasmuch as the loss on ignition method for the determination of organic matter as modified by Rather appeared to offer certain advantages from the standpoint of accuracy, a further study of the carbon content of soil organic matter seemed justifiable. It was our belief that the method for the simultaneous determination of soil organic matter and organic carbon would enable us to make a very accurate study of the percentage of carbon in the total organic matter of soils, and the investigation of a considerable number of representative soils was undertaken.

The results secured are recorded in tables 1, 2 and 3.

It may be observed from table 1 that the average percentage of carbon in the organic matter is 49.26, approximately 9 per cent lower than the conventional factor. If the lower values for the West Virginia soils are excluded, the general average becomes 51.93. None of the soils investigated contained as high as 58 per cent of carbon in the organic matter, the percentage variations extending from 30.20 to 56.27. These results show that the use of the 58 per cent factor uniformly gives low values and may lead to very erroneous conclusions. It is questionable whether the use of any carbon factor deserves recommendation, but if such a factor is to be employed one based on 50 to 52 per cent of carbon would be more reliable.

Table 2 shows the percentage of carbon in the organic matter of the corresponding sub- and sub-surface soils of table 1. The average percentage of

TABLE 1

Nitrogen and carbon determinations in surface soils

REGISTER NUMBER	SOIL TYPE AND LOCATION	DEPTH OF SAMPLE	ORGANIC MATTER	CARBON IN ORGANIC MATTER	NITROGEN IN ORGANIC MATTER
		inches	*per cent*	*per cent*	*per cent*
2654	Lamoure silty clay loam (Iowa)	0–20	6.18	54.78	5.22
2656	Webster silty clay loam (Iowa)	0–15	3.62	50.62	5.60
2658	Wabash silt loam (Iowa)	0–20	6.18	55.44	5.85
2660	Carrington loam (Iowa)	0– 8	4.20	54.26	6.76
2662	Fargo silty clay loam (Iowa)	0–18	6.82	53.53	5.26
2669	Shelby loam (Mo.)	0–10	1.71	50.67	7.60
2672	Decatur silt loam (Mo.)	0–10	1.68	47.07	7.68
2675	Grundy silt loam (Mo.)	0–12	2.70	52.93	7.67
2678	Marshall silt loam (Mo.)	0–12	2.37	50.07	6.84
2682	Summit silt loam (Kan.)	0– 7	4.07	53.54	6.41
2684	Laurel very fine sandy loam (Kan.)	0– 7	2.73	54.41	6.05
2686	Marshall silt loam (Kan.)	0– 7	2.68	53.42	6.90
2688	Wabash silty clay loam (Kan.)	0– 7	4.22	53.54	5.16
2690	Oswego silt loam (Kan.)	0– 7	5.59	53.32	5.06
2712	Fargo clay loam (Minn.)	0– 8	6.12	55.90	6.55
2714	Gloucester loam (Minn.)	0– 8	1.72	50.56	6.57
2716	Carrington silt loam (Minn.)	0– 8	4.22	49.92	5.88
2718	Hempstead silt loam (Minn.)	0– 8	3.76	54.43	5.61
2720	Colby silt loam (Wis.)	0– 7	1.91	48.77	6.23
2722	Clyde sandy loam (Wis.)	0– 7	3.70	54.54	6.17
2724	Clyde loam (Wis.)	0– 7	5.26	54.64	6.86
2726	Clyde silt loam (Wis.)	0– 7	4.56	52.67	6.10
2728	Superior silt loam (Wis.)	0– 7	2.00	44.61	7.05
2730	Waukesha silt loam (Wis.)	0– 7	1.23	44.38	9.84
2732	Knox silt loam (Wis.)	0– 7	2.18	45.21	7.16
2734	Westmoreland silty clay (W. Va.)	0– 7	5.40	50.49	5.89
2738	Upshur clay (W. Va.)	0– 7	2.73	30.20	4.73
2740	Moshannon silt loam (W. Va.)	0– 7	2.44	33.01	6.27
2742	Huntington loam (W. Va.)	0– 7	5.34	36.89	5.28
2744	DeKalb silt loam (W. Va.)	0– 7	2.47	37.56	5.91
2746	Tyler silt loam (W. Va.)	0– 7	2.44	40.34	6.39
2748	Wheeling silt loam (W. Va.)	0– 6	3.50	34.51	5.46
2760	Barnes loam (N. Dak.)	0– 7	6.18	55.87	5.95
2764	Fargo clay (N. Dak.)	0– 7	8.05	53.51	4.98
2766	Bearden silt loam (N. Dak.)	0– 7	5.46	55.08	6.52
2791	Diablo clay (Cal.)	0–12	3.30	56.27	5.55
2792	Diablo clay adoba (Cal.)	0–24	1.38	49.02	6.01
Average				49.26	6.24

carbon is 39.16 for the lower soil depths, and 43.91 for the entire list as given in tables 1 and 2. The range of percentage variation in table 2 is from 13.33 (Upshur clay subsoil) to 56.55, the value for the Wabash silt loam subsoil.

TABLE 2

Organic matter in the sub- and sub-surface soils of those recorded in table 1

REGISTER NUMBER	SOIL TYPE AND LOCATION.	DEPTH OF SAMPLE	ORGANIC MATTER	CARBON IN ORGANIC MATTER
		inches	*per cent*	*per cent*
2655	Lamoure silty clay loam subsoil (Iowa)	20–36	1.14	46.64
2657	Webster silty clay loam subsoil (Iowa)	15–36	1.22	47.16
2659	Wabash silt loam subsoil (Iowa)	20–36	2.19	56.55
2661	Carrington loam subsoil (Iowa)	18–36	0.94	48.41
2663	Fargo silty clay loam subsoil (Iowa)	18–36	3.46	52.14
2667	Putman silt loam subsurface soil (Mo.)	10–18	0.86	27.73
2668	Putman silt loam subsoil (Mo.)	18–36	0.90	29.36
2670	Shelby loam sub-surface soil (Mo.)	10–16	0.66	35.61
2671	Shelby loam subsoil (Mo.)	16–36	0.51	33.62
2673	Decatur silt loam sub-surface soil (Mo.)	10–20	0.75	26.72
2674	Decatur silt loam subsoil (Mo.)	20–36	0.46	22.82
2676	Grundy silt loam sub-surface soil (Mo.)	12–18	1.03	42.09
2677	Grundy silt loam subsoil (Mo.)	18–36	0.81	28.08
2679	Marshall silt loam sub-surface soil (Mo.)	12–24	1.68	35.46
2680	Marshall silt loam subsoil (Mo.)	24–36	1.03	28.04
2683	Summit silt loam subsoil (Kan.)	7–20	2.46	38.56
2685	Laurel very fine sandy loam subsoil (Kan.)	7–20	1.07	49.82
2687	Marshall silt loam subsoil (Kan.)	7–20	1.56	27.04
2689	Wabash silty clay loam subsoil (Kan.)	7–20	3.32	53.33
2691	Oswego silt loam subsoil (Kan.)	7–20	1.94	50.45
2713	Fargo clay loam subsoil (Minn.)	8–36	0.53	49.94
2717	Carrington silt loam subsoil (Minn.)	8–36	0.51	30.47
2719	Hempstead silt loam subsoil (Minn.)	8–36	0.55	29.96
2721	Colby silt loam subsoil (Wis.)	7–36	0.35	31.55
2723	Clyde sandy loam subsoil (Wis.)	7–36	0.44	53.93
2725	Clyde loam subsoil (Wis.)	7–36	1.16	51.14
2727	Clyde silt loam subsoil (Wis.)	7–36	1.32	48.44
2729	Superior silt loam subsoil (Wis.)	7–36	0.60	27.27
2731	Waukesha silt loam subsoil (Wis.)	7–36	0.49	30.29
2733	Knox silt loam subsoil (Wis.)	7–36	0.75	34.17
2735	Westmoreland silty clay subsoil (W. Va.)	7–20	3.46	43.71
2739	Upshur clay subsoil (W. Va.)	7–20	1.37	13.33
2741	Moshannon silt loam subsoil (W. Va.)	7–20	1.11	25.92
2743	Huntington loam subsoil (W. Va.)	7–20	3.08	35.53
2745	DeKalb silt loam subsoil (W. Va.)	7–20	1.02	20.83
2747	Tyler silt loam subsoil (W. Va.)	7–20	1.04	27.92
2761	Barnes loam subsoil (N. Dak.)	7–18	3.13	52.44
2765	Fargo clay subsoil (N. Dak.)	7–18	4.22	48.97
2767	Bearden silt loam subsoil (N. Dak.)	7–18	2.64	51.03
2790	Dublin clay subsoil (Cal.)	12–36	2.40	51.42
2793	Diablo clay adoba subsoil (Cal.)	24–72	1.08	42.42
Average				39.16

Table 3 presents data on 13 soils selected at random from table 1. The second column gives the actual percentage of organic matter found in these soils. The third, fourth and fifth columns show the percentage of organic matter calculated on the basis of 58 per cent carbon, 49.26 per cent carbon, and 6.24 per cent nitrogen, the average value found for the percentage of nitrogen in the organic matter of the surface soils. It is obvious from an inspection of the deviation values shown in table 3 that those in the fifth column are the least significant. On this basis, therefore, the adoption of a conventional nitrogen factor would seem to be more satisfactory and would make it possible to estimate the organic matter in soils more readily than by the organic carbon determination.

TABLE 3

Organic matter found in soils compared with calculated determinations

REGISTER NUMBER	ORGANIC MATTER FOUND	ORGANIC MATTER BASIS OF 58 PER CENT CARBON WITH DEVIATION	ORGANIC MATTER BASIS OF 49.26 PER CENT CARBON WITH DEVIATION	ORGANIC MATTER BASIS OF 6.24 PER CENT NITROGEN WITH DEVIATION
2654	6.18	5.86 −0.33	6.89 +0.71	5.17 −1.01
2660	4.20	3.94 −0.26	4.64 +0.44	4.55 +0.35
2712	6.12	5.82 −0.30	6.86 +0.74	6.42 +0.30
2720	1.91	1.61 −0.30	1.90 −0.01	1.91 ±0.00
2722	3.70	3.49 −0.21	4.11 +0.41	3.66 −0.04
2726	4.56	4.15 −0.41	4.89 +0.33	4.46 −0.10
2728	2.00	1.54 −0.46	1.82 −0.18	2.26 +0.26
2730	1.23	0.95 −0.28	1.12 −0.11	1.94 +0.71
2738	2.73	1.42 −1.31	1.68 −1.05	2.07 −0.66
2742	5.34	3.43 −1.91	4.04 −1.30	4.52 −0.82
2746	2.44	1.70 −0.74	2.00 −0.44	2.50 +0.06
2791	3.30	3.21 −0.09	3.78 +0.48	2.94 −0.36
2792	1.38	1.17 −0.21	1.38 ±0.00	1.33 −0.05
Average....	3.47	2.94	3.47	3.36

SUMMARY

An investigation of the carbon content of the organic matter of 37 surface soils secured from seven different experiment stations has been made by a modified rapid dry combustion method devised for the simultaneous determination of soil organic matter and organic carbon. Similar data also have been secured for the corresponding sub- and sub-surface soils.

The data presented show that the use of the generally accepted conventional factor uniformly gives low results.

The percentage of organic carbon in the surface soils varied from 30.20 to 56.27, the general average being 49.26, which is about 9 points below the accepted value.

It is very doubtful whether the use of any arbitrary carbon factor is justifiable. If one is to be employed more accurate results will be obtained if it is based on 50 to 52 per cent of carbon.

The data presented on the percentage of nitrogen indicate that the adoption of a conventional nitrogen factor would give more reliable information regarding the organic matter content of a soil, and certainly the nitrogen determination is more common and less difficult.

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THE RELATION OF HYDROGEN-ION CONCENTRATION IN SOILS TO THEIR "LIME REQUIREMENT"

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INTRODUCTION

Every state in the humid section of the United States is concerned with the acidity of soils. The nature of the phenomenon has not been understood and considerable controversy exists as to what constitutes this acidity. It has been attributed to the presence of acids, mineral and organic, to colloidal material, to adsorption and absorption, and to the presence of specific compounds. More recently the presence of hydrogen ions has been demonstrated. This is a property accompanying all acid reactions, hence their presence shows that soil acidity is actual acidity and is not a property due to the complicated theoretical phenomena previously advanced.

The presence of hydrogen ions has been demonstrated and their concentration has been measured by several investigators. Gillespie (5), using a hydrogen electrode, showed that of twenty-two samples tested, seventeen were acid and five alkaline, the pH values varying from 4.55 to 8.7. Sharp and Hoagland (18), using somewhat similar apparatus, studied twenty-four soils and found nine acid and fifteen alkaline with a variation in hydrogen-ion concentration of pH 3.7 to pH 9.7. Plummer (15) found a range of pH 4.04 to pH 9.68 in sixty-eight soils tested by the hydrogen electrode. Morse (14), in determining the hydrogen-ion concentration of different fertilizer plots by a colorimetric method, found that different fertilizers affected the acidity, sulfate of ammonia giving a pH value of 4.9 as compared with 5.2 for the check plot and 6.4 for a limed plot. Knight (12), using a hydrogen electrode, demonstrated the presence of hydrogen ions but in measuring his concentrations he used salt solutions, for some reason, so his measurements are not comparable with those of others.

Hydrogen ions may come from any of the organic or inorganic acids, from acid salts or from salts of weak bases and strong acids. Acid soils may contain all of these. The bases of the originally alkaline soils were converted into soluble salts by weathering and used by plants or leached out, leaving the less soluble acid silicates and silicates of iron and aluminum. Under these conditions nitric, sulfuric and many organic acids may accumulate from bacterial action. It is probable that the main sources of hydrogen ions are the acid silicates and the salts of the weak bases, iron and aluminum.

The diversity of opinions as to the nature of soil acidity has led to the formulation and adoption of numerous methods for its measurement. These different methods give such widely varying results that the correctness of any one of them is seriously in doubt. One investigator looks for "apparent acidity," another for "adsorption acidity," another for "real acidity," while all term their results "lime requirement."

Among the most widely adopted methods for the measurement of lime requirement are those of Hopkins (9), Veitch (24), and Tacke (20). These have all been modified by different workers so that there are now numerous methods based upon their principles. Two other methods should be noted also, one by Truog (21) because of its simplicity and practical applicability and another by Bouyoucos (2) because it measures not only the lime needed to neutralize the acidity but also the amount beyond this point which the soil will take up.

There are two general methods for the determination of hydrogen-ion concentrations in soils, one by the use of indicators and the other more accurate, by means of the hydrogen electrode. Gillespie (6), Wherry (25), and Van Altstine (23) have suggested colorimetric methods, including lists of indicators with their pH values, standard solutions and color comparators, especially applicable to soil studies. Such methods, while not so accurate as the hydrogen-electrode methods, are more rapid and probably of sufficient accuracy for many investigations. Almost as many forms of hydrogen electrodes have been devised as there are people working with them. They are compared with a great variety of standard electrodes, including many calomel and standard hydrogen cells and the electromotive force of such chains may be measured by several potentiometer methods and by more simple arrangements such as the one proposed by Hildebrand (7).

The comparative value of the two determinations, the lime requirement and the hydrogen-ion concentration, has not been fully determined. The lime-requirement methods have been in use for some time and a great amount of data is available to show that in general, when soils are found to need lime they are benefited by such applications, especially for certain crops, the legumes. This fact is so generally conceded that it is not necessary to discuss the matter. However, there are numerous cases where clover has been known to grow well on soils showing fairly high lime requirements and others where small applications of lime were as beneficial as larger ones.

Then, too, the wide variations in results by the different methods bring up the question as to what is the correct amount to apply in a definite case. The hydrogen-ion determination does not indicate the lime requirement directly but shows only the strength or intensity of the acidity. The methods for such determinations have been so recently put into use that no data are available as to its practical applications. A large amount of data has accumulated, however, to show that, in culture media, the strength of the acid and not the quantity present is the factor affecting bacterial and mold growth. Enzyme

activity also has been shown to be dependent on hydrogen-ion concentration. So positively is this proven that the adjustment of the reaction of such media is now made on this basis and not on the basis of titratable acid. Clark and Lubs (4) in 1917 collected and summarized sufficient data on this subject to prove the necessity of such adjustments. Many other workers have since shown conclusively their importance. If this is true of the lower organisms it is highly probable that the higher plants also are subject to the same factors. Wherry (25) makes the statement that, "Only the hydrogen ions developed directly by water in the soil can have any influence on the growth of plants." Hoagland (8) has studied the effect of hydrogen ions on the growth of barley seedlings and Joffe (10) their effect on alfalfa. Each found a range of hydrogen-ion concentrations which was favorable to the growth of the plants and concentrations on either side that were injurious.

From all of the foregoing considerations the question arises, "What is the relation between lime requirement as determined by the various methods and hydrogen-ion concentration?" If there is a definite relationship, as Blair and Prince (1) have shown to exist in the plots at the New Jersey station, we can interpret the data secured by lime requirement methods in terms of hydrogen-ion concentration. If there is no such relation, as might be indicated in the work by Joffe (11), then the inconsistencies of the data from lime requirement results may be explained.

In an attempt to answer this question lime requirement and hydrogen-ion conentration determinations have been made on fifty widely different soils. The results secured follow:

EXPERIMENTAL PROCEDURE

Fifty soils were selected from samples collected in connection with the soil surveys of seven different counties. Twenty-two different series inluding four different textures are represented, giving a wide variety of types for study. The types are listed in table 2.

The lime requirement of each sample was determined by both the Veitch and Truog methods. Hydrogen-ion concentrations were measured by the use of a hydrogen electrode.

The Veitch method was used because it has probably been more widely adopted and has been used as a standard for comparison of other methods more universally than any other of the lime requirement tests. It has been a standard method in this laboratory for several years.

The logical use of lime water in only sufficient amounts to bring about an alkaline reaction and the fact that results somewhat comparable with actual field tests are possible, have been just causes for its popularity. However, it has three serious disadvantages that have drawn to it very severe criticism. First, it is a long and tedious test applicable only in a laboratory; second, it shows only the amount of lime needed to give a reaction alkaline to phenol-

phthalein, an indicator which changes at a point quite toward the alkaline side of neutral; third, and very much the most serious disadvantage, it is so sensitive to very slight variations in its manipulation that it is almost impossible to obtain concordant results except by long and tedious trials so that the results obtained by two different workers can not be accurately compared. This last criticism has been demonstrated by Stephenson (19) and Robinson (16).

Considerable difficulty was encountered in this work in securing results which could be depended upon as correct. An attempt was made to determine the lime requirements to within 200 pounds, but this, except in cases of small requirements, was abandoned and a variation of 400 pounds was allowed with most samples and even 800 pounds with soils showing need for

TABLE 1

Illustrating the difficulty in securing duplicate tests with the Veitch method

SOIL NUMBER	LIME WATER*	REACTION	LIME WATER	REACTION	LIME WATER	REACTION	LIME WATER	REACTION	LIME WATER	REACTION	LIME WATER	REACTION	LIME WATER	REACTION	LIME WATER	REACTION	LIME WATER	REACTION
	cc.		*cc.*		*cc.*		*cc.*		*cc.*		*cc.*		*cc.*		*cc.*		*cc.*	
	10	Acid	8	Acid	8	Acid	9	Acid	10	Acid	10	Acid	11	Alk.	10	Acid		
15	15	Alk.	12	Alk.	10	Acid	10	Acid	11	Acid	11	Acid	12	Alk.	11	Alk.		
	20	Alk.	16	Alk.	12	Alk.	11	Acid	12	Alk.	12	Acid	13	Alk.	12	Alk.		
	10	Acid	20	Acid	16	Acid	18	Acid	18	Acid	18	Acid	18	Acid	19	Alk.	19	Acid
23	15	Acid	25	Alk.	20	Alk.	20	Acid	19	Alk.	19	Acid	19	Acid	20	Alk.	20	Alk.
	20	Acid	30	Alk.	24	Alk.	22	Acid	20	Alk.	20	Alk.	20	Acid	21	Alk.	21	Alk.
	25	Alk.	15	Acid	18	Acid	22	Acid	24	Acid	24	Alk.	23	Acid	23	Acid		
30	30	Alk.	20	Acid	22	Acid	24	Acid	26	Acid	26	Alk.	24	Acid	24	Acid		
	35	Alk.	25	Alk.	26	Alk.	26	Acid	28	Acid	28	Alk.	25	Alk.	25	Alk.		

*Each cubic centimeter of lime water is equivalent to 200 pounds of limestone, $CaCO_3$ per acre of 2,000,000 pounds of soil.

the largest amounts of lime. Apparently good results could be secured easily but attempts to duplicate the test frequently failed. Results in table 1 illustrate the difficulties encountered in checking tests with three representative samples.

In all the work double-distilled water was used and extreme care was taken to see that all manipulations were as nearly the same as possible at all times.

The results reported in table 2 and used throughout this article were accepted only after repeated trials, as shown in the above table, had proved their accuracy.

The Truog test was compared with the hydrogen-ion determinations because it has largely supplanted the Veitch method at this station for routine analyses and tests for field applications. It is also widely used for practical tests out-

side of the experiment stations. The lime requirements reported in table 2 are results of two agreeing tests.

The hydrogen-ion determinations were made with a hydrogen electrode, patterned after the one used by Sharp and Hoagland (18), modified slightly as shown in figure 1, A. The platinum electrode consists of a $\frac{3}{8}$-inch square of heavy platinum foil coated with platinum black deposited from a 3 per cent solution of platinic chloride containing a trace of lead acetate. Two hydrogen electrodes were held in a shaking device, as illustrated in figure 1 B, which was operated by an electric motor regulated so as to give between 160 and 180 complete strokes, $\frac{3}{4}$-inch long, a minute. Hydrogen was generated electrolytically and purified by passing over heated, platinized asbestos. Connection was made to a normal calomel electrode through a saturated potassium chloride solution by means of a tube filled with agar made up with a saturated potassium chloride solution.

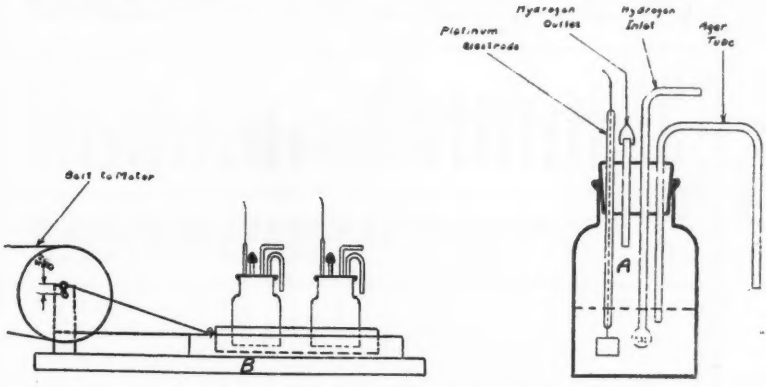

FIG. 1. HYDROGEN ELECTRODE AND SHAKER

The electromotive force of the chain was measured by an apparatus as suggested by Hildebrand (7), using an accurate voltmeter calibrated from 0 to 1.5 volts by intervals of .01 volt and readable to 2 millivolts. Ten grams of soil with 25 cc. of neutral water were used for the determinations. Readings on duplicate samples checked to within 5 millivolts in every case and frequently checked exactly. The accuracy of the determinations is within .05 of a pH value.

The hydrogen-ion concentrations of the fifty samples are reported in table 2 in pH values, a term which has been used so much of late that there is no necessity for its explanation here. However, Schmidt and Hoagland (17), Clark and Lubs (4) and Leeds and Northrup (13) explain in detail the method by which it is obtained. It should be remembered that 7.0 pH is neutral and that a lower pH value shows acidity, corresponding to a higher hydrogen-ion concentration, while a greater value means alkalinity with a correspondingly lower hydrogen-ion concentration.

TABLE 2

Results of Veitch, Truog and hydrogen-ion determinations and analyses of soils on basis of acre of 2,000,000 pounds

NUMBER	SOIL TYPE	VEITCH LIME REQUIREMENT	TRUOG LIME REQUIREMENT	(H^+) IN ^pH	ORGANIC CARBON	NITROGEN	CARBON – NITROGEN RATIO, N=1	PHOSPHORUS
		lbs.			*lbs.*	*lbs.*		*lbs.*
1	Sarpy loam	0	negative	7.78	22,700	1,980	11.4	2,195
2	Thurston sandy loam	0	negative	7.73	20,500	1,180	17.4	1,185
3	Sarpy silt loam	0	negative	7.68	29,983	2,590	11.6	1,481
4	Wabash silt loam	0	negative	7.56	53,631	4,180	12.8	1,669
5	Carrington sandy loam	0	negative	7.54	30,977	2,630	11.8	1,024
6	Cass fine sandy loam	0	negative	7.30	27,237	1,770	15.4	808
7	Jackson silt loam	0	negative	7.20	29,721	2,370	12.4	660
8	Clyde silty clay loam	0	negative	7.05	17,581	890	19.8	593
9	Wabash loam	0	very slight	6.86	46,137	3,800	12.2	822
10	Carrington loam	600	very slight	6.41	60,060	4,800	12.5	1,091
11	Lindley fine sandy loam	800	very slight	5.83	13,377	1,120	12.0	485
12	Hancock loam	1,600	slight	6.88	75,238	5,650	13.6	902
13	Carrington loam	2,000	strong	5.70	27,627	2.380	11.6	902
14	Knox fine sandy loam	2,000	slight	4.85	10,592	720	14.7	942
15	Lindley sandy loam	2,200	medium	5.33	12,175	890	13.7	687
16	Lindley loam	2,400	slight	5.51	23,478	1,740	13.5	745
17	Plainfield loam	2,800	slight	5.39	21,294	1,310	16.3	808
18	Cass sandy loam	3,000	medium	5.34	19,929	1,120	17.8	1,010
19	Buckner fine sandy loam	3,000	strong	5.02	37,128	3,090	12.0	889
20	Wabash silt loam	3,200	negative	7.30	38,493	2,980	12.9	1,736
21	Plainfield sandy loam	3,200	medium	5.36	23,641	1,340	17.6	808
22	Wabash fine sandy loam	4,000	slight	6.36	73,381	5,500	13.4	1,913
23	Carrington fine sandy loam	4,000	medium	5.38	37,401	2,740	13.7	943
24	Shelby loam	4,200	very strong	5.41	27,027	2,210	12.2	795
25	Shelby loam	4,400	strong	5.53	36,145	2,960	12.2	889

26	Carrington sandy loam	4,400	very strong	5.02	28,665	1,960	14.6	741
27	Carrington silt loam	4,800	medium	6.04	43,680	3,670	11.9	1,387
28	Buckner loam	4,800	very strong	5.53	52,962	3,950	13.4	1,131
29	O'Neill loam	4,800	strong	5.04	33,688	3,700	9.1	1,428
30	O'Neill sandy loam	5,000	very strong	5.00	25,880	1,460	17.7	876
31	Lindley silt loam	5,200	slight	5.90	27,846	2,070	13.4	660
32	Clinton silt loam	5,200	medium	5.33	19,110	1,760	10.8	700
33	Waukesha silt loam	6,800	medium	6.00	46,137	3,480	13.2	1,495
34	Judson silt loam	7,600	medium	5.73	49,140	3,600	13.7	1,414
35	Carrington loam	7,600	strong	5.36	48,590	4,180	11.6	1,050
36	Marshall silt loam	8,400	medium	5.58	53,344	4,360	12.2	929
37	Tama silt loam	8,800	slight	5.36	36,036	2,520	14.3	902
38	Bremer silt loam	9,600	medium	6.20	107,452	8,380	12.8	2,074
39	Clinton silt loam	9,600	slight	5.53	34,343	2,680	12.8	1,100
40	Clinton silt loam	9,600	medium	5.36	33,961	2,730	12.5	996
41	Carrington loam	10,800	very strong	5.11	50,641	4,410	11.5	1,024
42	Grundy silt loam	11,200	medium	5.66	96,587	4,860	20.0	1,118
43	Grundy silt loam	12,000	strong	5.11	56,511	4,160	13.6	1,387
44	Carrington loam	12,800	very strong	5.14	62,244	5,190	12.0	1,145
45	Tama silt loam	12,800	strong	4.94	54,873	4,480	12.3	1,414
46	Putnam silt loam	12,800	very strong	4.84	34,944	2,820	12.4	969
47	Tama silt loam	13,600	medium	5.19	59,623	4,600	13.0	1,306
48	Wabash silt loam	14,400	strong	5.22	42,970	3,530	12.2	983
49	Wabash loam	18,000	strong	5.56	113,677	9,590	11.9	1,913
50	Bremer loam	24,000	very strong	4.55	76,767	6,200	12.4	1,684

EXPERIMENTAL RESULTS

In table 2 and graphically in figure 2 is shown the relation of the hydrogen-ion concentrations to the Veitch lime requirement of each of the fifty samples. The samples have been arranged in the table and for making up the graph in the order of increasing Veitch lime requirement. Where samples show the same lime requirement the one having the highest pH value is given first.

It will immediately be noted that there is no apparent relationship between the results of the two determinations except that all of the samples having no lime requirement, except no. 9, show an alkaline reaction as measured by the hydrogen electrode and all of the samples with lime requirements, except no. 20, show acid with the electrode. It was found that the soils with a low

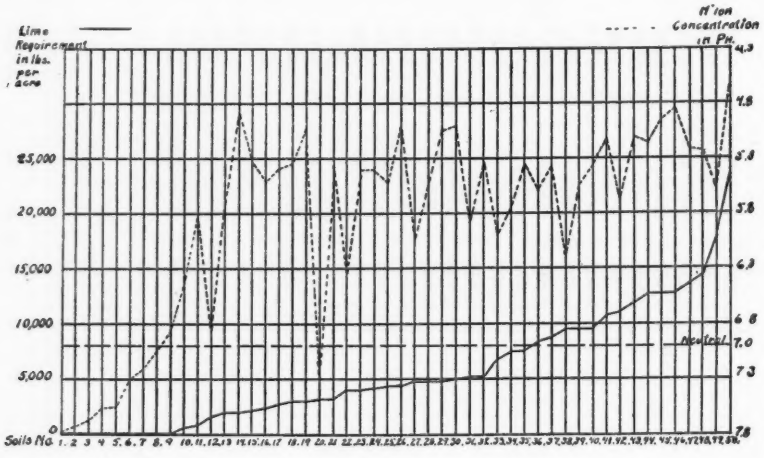

FIG. 2. RELATION OF VEITCH LIME REQUIREMENT TO HYDROGEN-ION CONCENTRATION

lime requirement had as high a hydrogen-ion concentration as those in need of the larger amounts of lime, in fact no. 14, with a lime requirement of only 2000 pounds has the highest hydrogen-ion concentration of all the samples except no. 50. Even the general trend of the line representing hydrogen-ion concentrations bears no relation to the line representing lime requirement. It is evident that in considering soils of different types there is no relation between acidity, as measured by the hydrogenelectrode, and so-called "acidity," as measured by the Veitch method.

In table 2 and figure 3, the results of Truog tests as related to hydrogen-ion concentrations are shown. In figure 3 as in figure 2, the samples are arranged in order of increasing lime requirement. This was done by laying the test papers in a row and arranging them according to the intensity of color. The arrangement was checked by three other observers. The points on the

curve indicating very slight, medium, strong and very strong acidity were determined by selecting the test papers corresponding to the colors on the Truog chart (21). Lines connecting these points, representing the acidity of intervening samples, give a fairly regular curve for the Truog tests.

From figure 3 it is evident that here again there is no definite relationship between the results obtained by the Truog test and the hydrogen electrode. It will be noted, however, that there is somewhat better correlation than in figure 2. All the samples with no lime requirement show alkaline by the electrode method and all those in need of lime show acid. Also it is very evident that the general trend of the hydrogen-ion line is more nearly parallel to the Truog test line than it was to the Veitch test line. Apparently the Truog method has more of a tendency to indicate the strength of the acids than has the Veitch test.

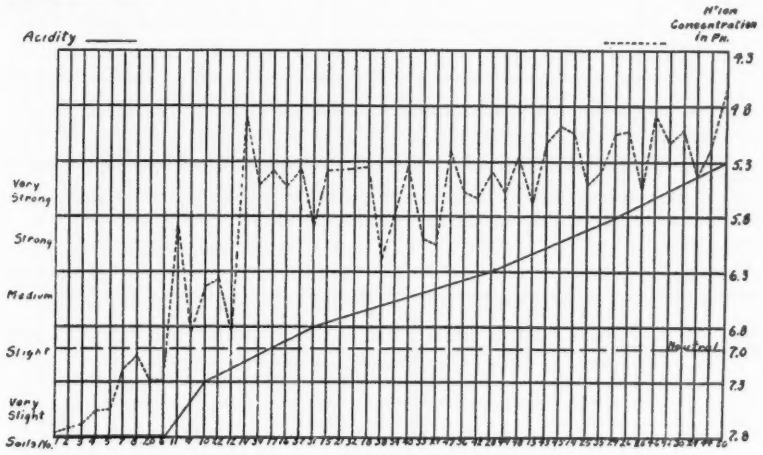

FIG. 3. RELATION OF TRUOG ACIDITY TO HYDROGEN-ION CONCENTRATION

Considering both tests, however, the conclusion is necessarily reached that lime requirement is not very closely related to the strength of the soil acids when soils of various types are compared. When this lack of relationship became evident an explanation for it was sought.

The soils were separated into four classes, silt loams, loams, fine sandy loams and sandy loams according to texture. One silty clay loam, no. 8, was included with the silt loams. The samples in each class were arranged according to increasing lime requirements by both methods and plotted in figures 4 and 5. It is readily seen from these diagrams that texture has a great influence on the relation between the lime requirement and hydrogen-ion concentration. With the finer textured soils the trend of the lines representing the two determinations is nearly parallel and the lines are not far apart. This is especially true of the Truog tests. It will be noted, too, that the finer

soils include the ones with the higher lime requirement. In the case of the coarser textured samples the lines are very far apart. These have rather low lime requirement but very high hydrogen-ion concentration. Even though

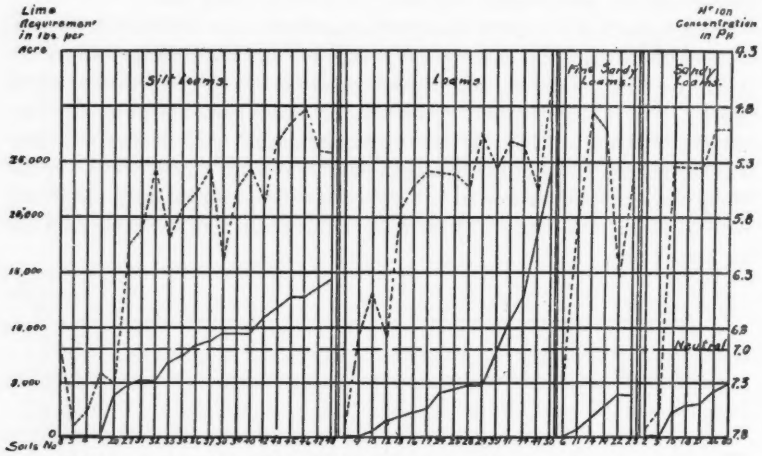

FIG. 4. RELATION OF VEITCH LIME REQUIREMENT TO HYDROGEN-ION CONCENTRATION AS AFFECTED BY SOIL TEXTURE

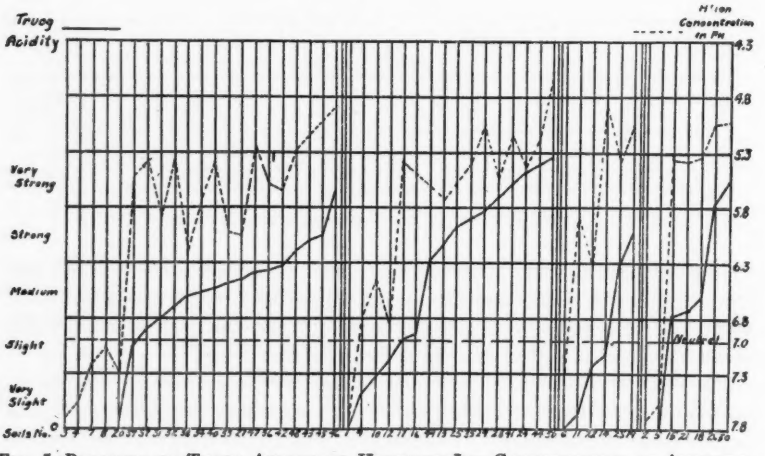

FIG. 5. RELATION OF TRUOG ACIDITY TO HYDROGEN-ION CONCENTRATION AS AFFECTED BY SOIL TEXTURE

texture explains some of the irregularities in the relationship between the two determinations, there is evidently some other factor which has even greater influence, since the line representing hydrogen-ion concentration is still very uneven. This is quite pronounced in the case of both tests.

When a line representing the organic carbon content[1] of each soil is drawn in, as in figure 6, the influence of organic matter on the intensity of the acidity is very evident. When the organic matter content is very low, the hydrogen-ion concentration is very high and when the organic content runs very high the hydrogen-ion concentration as compared to the lime requirement is very low. These relationships are very strikingly true in samples 12, 14, 15, 18, 22, 32, 38, 42, 46 and 49.

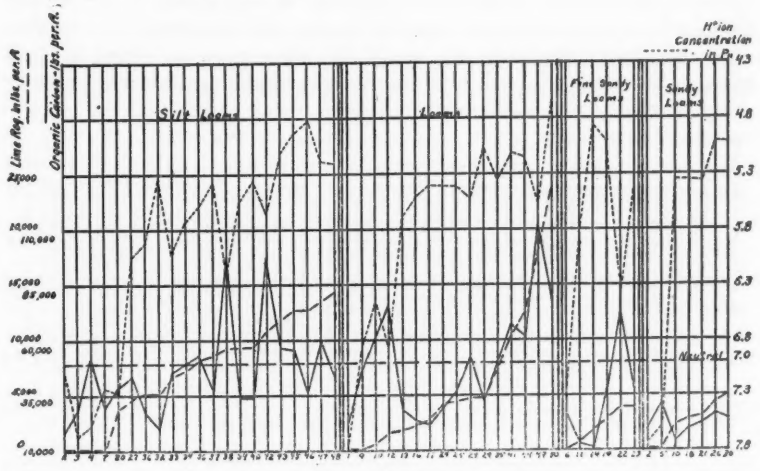

FIG. 6. RELATION OF VEITCH LIME REQUIREMENT AND HYDROGEN-ION CONCENTRATION IN SOILS OF SIMILIAR TEXTURE TO ORGANIC CARBON CONTENT

DISCUSSION OF RESULTS

From the brief outline of results given, it is evident that the Veitch method does not in any way indicate the intensity of the acidity. It may measure the amount of lime which will be taken up by a soil but this seems to have little relation to the strength of the soil acids. The Truog test in a slight measure does indicate the strength of the acids. In figure 7 the Veitch, Truog and hydrogen-ion determinations are plotted together. From this graph it seems that the results of the Truog test are a combination of the other two determinations. With low lime requirement and high hydrogen-ion concentration, the Truog test shows a higher lime requirement than the Veitch, and the opposite is true. Truog (22) has demonstrated this by the use of his acidity method and claims a superiority for practical use for his test in that it gives what he terms "crop-injurious acidity."

[1] The analyses of these soils were made by Mr. J. T. Auten for the Soil Survey reports; the author wishes to express his appreciation to Mr. Auten for the use of his results.

That soil acids do not accumulate in the coarser textured soils to so great an extent as in the heavier soils but that those that are present are stronger, is clearly shown. Both the amount and strength of the acids present can be explained by the content of clay and silt particles in the individual soils. These particles are made up of the more finely divided silicates, hence are more readily weathered to form large quantities of acid silicates which can react with lime water to show apparent acidity. The coarser material of the lighter soils is not so subject to weathering, as was shown by Brown and Johnson (3) who found that grinding the coarser soils reduced the lime requirement; thus acid silicates do not accumulate to so great an extent in these lighter soils. Then too, much of the coarse material consists of silica, SiO_2,

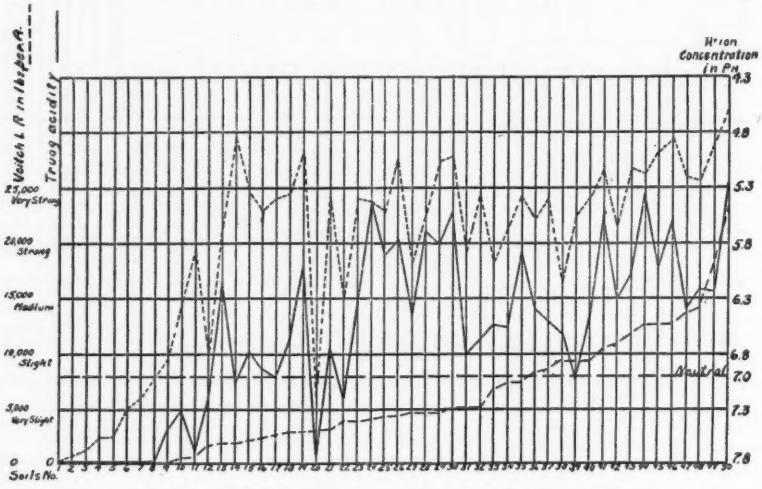

FIG. 7. RELATION OF VEITCH, TRUOG AND HYDROGEN-ION DETERMINATIONS

which is too inert to react with lime water. Hence the greater source of potential acidity is found in the heavier soils.

On the other hand, the quantity of fine material present affects the strength of the acids in two ways. First, it is a recognized fact that coarser, more open soils are more easily and rapidly weathered and leached than the heavier soils. Thus the bases in the finer particles in the sandy soils will be more nearly completely removed than in the finer textured soils. This would affect the strength of the soil acidity in that the degree of removal of base would determine the amount of hydrogen-ions liberated. This may be illustrated by the titration curve for phosphoric acid where each of the acid salts, KH_2PO_4 and K_2HPO_4, gives rise to a definite hydrogen-ion concentration as is shown by Clark and Lubs (4). Thus the different acid salts formed in the weathering of the silicates would give rise to different hydrogen-ion concentrations; the less the amount of base present in each molecule the more intense would be

the acidity. Hence, with sandy soils which would be more highly weathered, we would expect a higher hydrogen-ion concentration.

The second effect might be due to "buffer" action of the clay. Several acid salts show this property, an ability to resist changes in hydrogen-ion concentration on the addition of acids or alkalis. This, too, is illustrated by the action of the phosphate salts in the experiment referred to above. When either of the acid phosphates are present, additions of potassium hydroxide have little effect on the pH value of the solution until all the salt present is changed over to another form. In soils the acid silicates may act as "buffers." This effect would be proportional to the amount of silicates present and their degree of weathering, which in turn would depend on the texture of the soil. In a soil containing more clay, consequently more silicates in a less weathered condition, the buffer effect would be greater. Hence, the accumulation of nitric, sulfuric and organic acids, and even the greater weathering and consequent hydrogen-ion liberation of some of the soil particles, would affect the hydrogen-ion concentration of the heavier soils less than the sandier ones.

The influence of the organic matter also may be explained by its "buffer" action. Organic materials are known to possess a very considerable "buffer" action, as has been shown by Clark and Lubs (4). Thus, with soils containing the larger amounts of organic carbon, we would expect to find the hydrogen-ion concentration very markedly depressed, while with smaller quantities no such effect would be obtained.

The older statements, that soil acidity was due entirely to organic acids, seem to be quite definitely discredited by these results, since the larger amounts of organic matter depress rather than increase the acidity. These statements are further contradicted when the carbon-nitrogen ratio, a widely adopted measure of the decomposition of organic matter, is plotted against the acidity, as in figure 8. It is very evident that the carbon-nitrogen ratio bears no relation to the acidity, hence, the oxidation of the organic matter with the supposedly consequent accumulation of organic acids can not be a cause of soil acidity in these soils. It must be noted, however, that these are mineral soils and the same would not hold true for peats and mucks.

Since the acidity could not be explained by the presence of organic acids, it was sought to prove it was due to weathering and subsequent removal of bases. The only index to such action available at present was the phosphorus content. This is only a rough index and its value was recognized as questionable. However, in these soils, all formed from similar materials, although laid down by different agencies at different times, the amount of phosphorus present should be, in general, proportionate to their loss of bases. Plotting this against the acidity and knowing it could in no way be a cause for acidity but only an approximate index to the cause in soils of similar texture, the results as shown in figure 9 were obtained. Here it is seen that where the phosphorus content is high, showing supposedly less weathering and loss of bases, the intensity of acidity is much less. This not only indicates that soil

acidity is due to weathering with subsequent loss of bases and the consequent formation of acid silicates, but substantiates the reasons given previously as to why the coarser soils are more intensely acid than the finer ones.

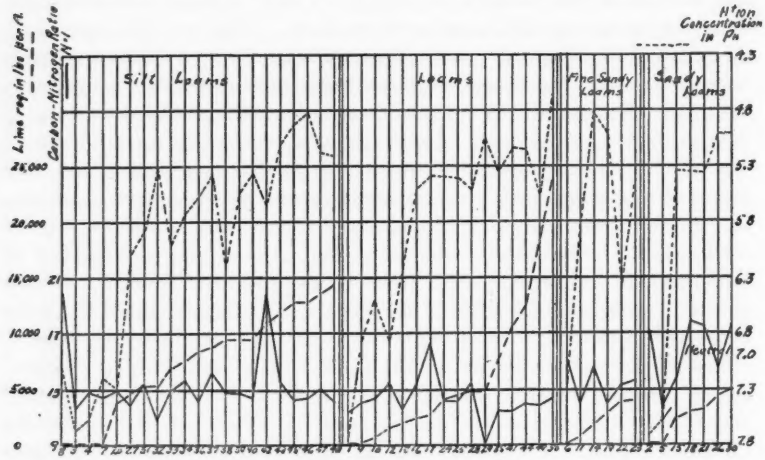

FIG. 8. RELATION OF VEITCH LIME REQUIREMENT AND HYDROGEN-ION CONCENTRATION IN SOILS OF SIMILIAR TEXTURE TO CARBON-NITROGEN RATIO

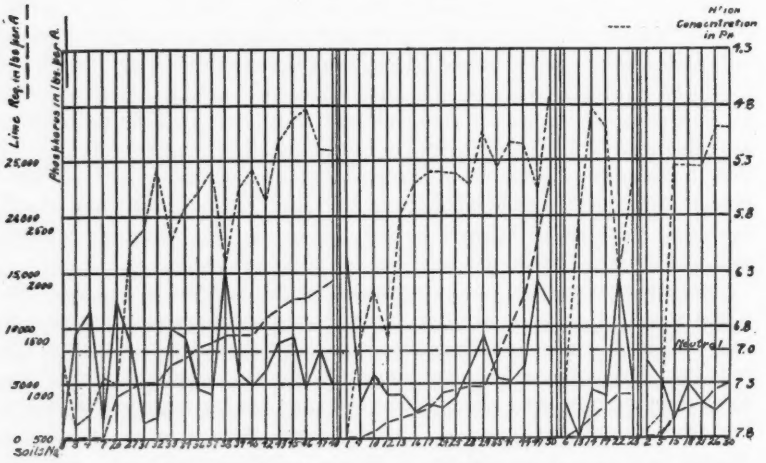

FIG. 9. RELATION OF VEITCH LIME REQUIREMENT AND HYDROGEN—ION CONCENTRATION IN SOILS OF SIMILAR TEXTURE TO PHOSPHORUS CONTENT

From all these considerations, it is plainly evident that, in soils as a whole, the apparent quantity of acid or the lime requirement has no relationship to the intensity or strength of acids present or the hydrogen-ion concentration.

This substantiates the inferred conclusions of Joffe (11) that sands and clays vary in relation between these two factors. However, for soils of the same type, that is, the same texture, age, formation, and color or organic-matter content, the two factors may bear a close relationship to each other. This explains the conclusions of Blair and Prince (1) who found that there was a definite relation between the lime requirement and hydrogen-ion concentration, working on the series of plots at the New Jersey station.

SUMMARY

Working with fifty samples of widely varying types it was found that:

1. As a whole there was no relation between the lime requirement as determined by the Veitch method and the hydrogen-ion concentration as measured by the hydrogen electrode.
2. The Truog method of measuring the lime requirement gave results which were a combination of the Veitch lime requirement and the hydrogen-ion concentration.
3. In soils of similar type there is a relation between the apparent quantity of acids and the strength of the acids.
4. Soil acidity in mineral soils is apparently due to weathering and leaching rather than the accumulation of organic acids.
5. Clay particles and organic matter act as "buffers" to keep the hydrogen-ion concentration down.

The buffer effect of these two materials is being further studied, as is also the proof of the statement that soil acidity is due to the weathering and leaching and consequent formation of acid silicates.

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ALUMINUM SALTS AND ACIDS AT VARYING HYDROGEN-ION CONCENTRATIONS, IN RELATION TO PLANT GROWTH IN WATER CULTURES

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INTRODUCTION

While there is a rather extensive literature upon the subject of the injurious effect of various acids and of aluminum salts upon plants in water cultures, there are so many variables which may affect plant growth that it is difficult to correlate the results obtained by different investigators. One of the factors which may cause a great variation in growth is the kind of nutrient solution and the method of using it. Without doubt this factor is one of the most important. There are very many combinations of various salts, proportions, and strengths which have been used, as well as sizes of containers and periods of frequency of changing the nutrient—all of which may vary the results obtained. The purity of the distilled water as well as that of the salts varies greatly. The kind of plant grown, the uniformity of the seed, and its freedom from, or affection by, disease may often cause variation in results.

Abbott, Conner and Smally (1) found in 1913 that solutions of aluminum nitrate and nitric acid were toxic to corn seedlings in dilute nutrient solutions. The toxicity of the aluminum nitrate was found to be approximately equal to that of nitric acid of the same normality. They suggested that the acid radical might be the toxic agent. Miyake (6) in 1916, in a study of the effect of aluminum chloride and hydrochloric acid on the rice plant in distilled water, found that the toxicity of aluminum chloride was equal to that of hydrochloric acid of the same normality. He determined the hydrogen-ion concentration of the solutions and found that the aluminum salt was more toxic than the acid at the same hydrogen-ion concentration and concluded that aluminum itself in some way was toxic. Hartwell and Pember (3) in 1918, after considerable work to find a suitable nutrient, found that, while aluminum sulfate was of equal toxicity toward rye as was sulfuric acid, barley was much more affected by aluminum salts than by an acid of the same hydrogen-ion concentration. They concluded that the toxicity of aluminum salts on barley is attributable largely to the aluminum.

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EXPERIMENTAL

With the object in view of investigating the relative toxicity of hydrogen ions and aluminum ions in a series of water cultures with aluminum salts and their corresponding acids, under controlled conditions, with seedlings of several cereals, experiments were started in 1919. In a first series of tests the grain was germinated in white moist silica sand, then washed and transferred to wide-mouth bottles of 480 cc. capacity. Paraffined cork stoppers were grooved on the sides and three seedlings held in place by rubber bands. In some preliminary tests the barley seedlings were partially affected by *helminthosporium* and *fusarium* enough to confuse the results. Rye and corn also were more or less affected by *fusarium* and other fungus diseases. In later tests the rye and corn were sterilized in dilute silver nitrate, then washed in water, in sodium chloride solution, and again rinsed. This almost entirely prevented any infection. The barley used in later tests through the courtesy of the Wisconsin Experiment Station, was given a hot-air treatment of 24 to 30 hours. This almost entirely prevented infection by *helminthosporium* and at the same time caused no injury to germination. With the later tests 2100 cc. wide-mouth jars were used and the seedlings were supported by cotton in $\frac{1}{4}$-inch holes cut with a cork borer in the edge of the wide, flat, paraffined corks. Germination was made in large jars of tap-water over which was stretched paraffined mosquito netting.

The first series of tests on rye, pop corn, and barley were grown in duplicate in Tottingham's (8) sub-optimiun solution, 480-cc. bottles were used and the nutrient changed weekly. The results of these tests are shown in table 1.

Both top and root weights are the relative total dry weights of the duplicate sets of six plants. A study of these results show that for barley as well as rye, the aluminum salts have given higher average yields than the acids. With pop corn there was a tendency for the aluminum salts to reduce the yield more than the acids did. These results are not believed to be significant, because the nutrient used was later shown not to be suited to show this point and equivalent pH values were not held in acids and aluminum salts.

If the results are averaged according to acid groups, there is little difference among the strong acids. The plants grown with sulfuric acid show slightly the lowest weights, then hydrochloric acid, nitric acid, phosphoric acid and tartaric acid follow in order. Tartaric acid tended to average higher than any of the mineral acids or their aluminum salts. A correlation of the pH values before and after growth, shows that in every case where there was a good growth of barley the hydrogen-ion concentration was markedly lowered. This change in pH value occurred in the N/4800 concentrations of the strong acids and their aluminum salts only. It occurred with the N/2400 as well as the N/4800 phosphoric acid solutions, and with all solutions of tartaric acid or aluminum tartrate. This is in accord with the results reported by Hoagland (4).

TABLE 1

Growth of rye, barley and pop corn in Tottingham's nutrient solution, May, 1919

NUMBER	TREATMENT	pH VALUE OF SOLUTION		WEIGHT OF PLANTS RELATIVE TO CHECK		
		Beginning	End	Rye	Barley	Corn
				per cent	*per cent*	*per cent*
1	Check	6.4	6.5	100	100	100
2	HNO_3 N/600	2.9	2.9	29	17	77
3	HNO_3 N/1200	3.1	3.1	41	24	53
4	HNO_3 N/2400	3.4	3.5	71	34	105
5	HNO_3 N/4800	3.6	6.3	73	65	186
6	$Al(NO_3)_3$ N/600	3.9	3.7	52	33	51
7	$Al(NO_3)_3$ N/1200	3.9	3.8	65	33	39
8	$Al(NO_3)_3$ N/2400	4.0	3.9	70	42	63
9	$Al(NO_3)_3$ N/4800	4.1	6.4	69	65	103
10	H_2SO_4 N/600	2.9	2.9	28	19	48
11	H_2SO_4 N/1200	3.1	3.1	32	25	61
12	H_2SO_4 N/2400	3.4	3.5	57	34	144
13	H_2SO_4 N/4800	3.7	6.3	97	53	136
14	$Al_2(SO_4)_3$ N/600	3.9	3.9	56	28	38
15	$Al_2(SO_4)_3$ N/1200	3.9	4.0	53	34	58
16	$Al_2(SO_4)_3$ N/2400	4.0	4.0	63	31	77
17	$Al_2(SO_4)_3$ N/4800	4.1	6.3	56	45	126
18	HCl N/600	2.9	2.9	20	21	41
19	HCl N/1200	3.1	3.1	29	23	70
20	HCl N/2400	3.4	3.5	61	35	85
21	HCl N/4800	3.7	6.4	78	63	93
22	$AlCL_3$ N/600	3.8	3.8	54	34	49
23	$AlCL_3$ N/1200	3.9	3.9	84	37	55
24	$AlCL_3$ N/2400	3.9	4.0	81	42	49
25	$AlCL_3$ N/4800	4.0	6.7	57	69	79
26	Tartaric Acid N/600	3.1	5.9	29	29	42
27	Tartaric Acid N/1200	3.4	6.4	61	42	60
28	Tartaric Acid N/2400	3.5	6.4	101	77	77
29	Tartaric Acid N/4800	3.8	6.5	132	87	115
30	Aluminum Tartrate N/600	3.9	6.5	96	43	110
31	Aluminum Tartrate N/1200	4.1	6.8	91	75	107
32	Aluminum Tartrate N/2400	4.1	6.5	74	92	239
33	Aluminum Tartrate N/4800	4.2	6.5	72	89	92
34	$Al_2(SO_4)_3$ N/600 + H_3PO_4 N/600	3.0	4.1	32	24	44
35	$Al_2(SO_4)_3$ N/600 + $CaH_4(PO_4)_2$ N/600	3.3	3.4	48	27	54
36	$Al_2(SO_4)_3$ N/600 + $Ca_2H_2(PO_4)_2$ N/600	3.6	3.6	53	33	86
37	$Al_2(SO_4)_3$ N/600 + $Ca_3(PO_4)_2$ N/600	4.0	5.3	56	56	119

TABLE 1—*Concluded*

NUMBER	TREATMENT	pH VALUE OF SOLUTION		WEIGHT OF PLANTS RELATIVE TO CHECK		
		Beginning	End	Rye	Barley	Corn
				per cent	*per cent*	*per cent*
38	$Al_2(SO_4)_3$ N/600 + H_2SiO_3 N/600	3.8	3.8	77	26	52
39	$Al_2(SO_4)_3$ N/600 + $CaSiO_3$ N/600	3.9	4.2	72	33	75
40	$Al_2(SO_4)_3$ N/600 + $CaCO_3$ N/600	4.3	7.0	50	55	63
41	$Al_2(SO_4)_3$ N/600 + $MgCO_3$ N/600	4.0	4.3	61	39	47
42	$Al_2(SO_4)_3$ N/600 + Dextrose 0.1 gm	3.9	4.0	58	died	died
43	$Al_2(SO_4)_3$ N/600 + Mannit 0.1 gm	4.0	4.1	53	died	34
44	$Al_2(SO_4)_3$ N/600 + Glycerine 0.1 gm	4.1	4.2	52	died	40
45	$Al_2(SO_4)_3$ N/600 + Carbon Black 0.1 gm	3.8	4.0	82	36	43
46	H_3PO_4 N/600	3.2	3.5	56	35	45
47	H_3PO_4 N/1200	3.6	4.1	45	42	98
48	H_3PO_4 N/2400	3.9	6.3	44	79	136
49	H_3PO_4 N/4800	4.2	6.4	69	86	76
50	H_2SO_4 N/600 + $CaCO_3$ N/600	3.6	6.9	none	99	200

Total dry weights of roots and tops on checks:
6 rye plants, 3 weeks old ..... 0.531 gm.
6 barley plants, 3 weeks old ..... 0.896 gm.
4 pop corn plants, 4 weeks old ..... 0.254 gm.
Hydrogen-ion concentration was taken by colorimetric method at beginning and end of test on barley.

The only supplementary treatments which caused good growth in barley were those that decreased the hydrogen-ion concentration. It should be noted, however, that calcium carbonate was of much greater benefit in reducing the toxicity of sulfuric acid than it was in correcting the aluminum sulfate injury, although it corrected the acidity in both solutions. In some of the results on corn shown in table 1, as well as in some preliminary work with barley, the nutrient checks did not show as good growth as the treatments of weaker acids and aluminum salts. This was thought to be due at least partly to lack of available iron. For the same reason the N/4800 aluminum-salt rye cultures were inferior to those containing more aluminum. In the later tests, citrate of iron was substituted for phosphate of iron with satisfactory results. These results are in accord with the work of Jones and Shive (5) and others who have found that iron is a more important ingredient in nutrient solutions than earlier investigators thought.

Plate 1 shows the relative growth of rye, pop corn, and barley with sulfuric acid and aluminum sulphate of equivalent normality. The rye roots show a greater tolerance toward aluminum salts than either pop corn or barley. The difference in top growth is not so apparent.

It was thought, from the first year's work, that it would be necessary to devise some method of holding the hydrogen-ion concentration constant, before definite conclusions could be reached. A constant flow of nutrient was tried in a tentative test without success. The flow of nutrient was regulated by Hofmann pinchcocks. This test was a failure on account of inability to secure an equal flow in all bottles. To regulate this condition 2100-cc. bottles were used and the nutrient changed daily instead of weekly.

Barley was grown in Shive's (7) R_4C_5 sub-optimum nutrient solution in the next test. Glass bottles of 2100 cc. capacity were used and the nutrient changed daily except at the end of the test when the changes in pH values of the solutions were noted. Nutrients of 0.025, 0.1, and 0.4 atmospheres osmotic pressure and sulfuric acid of four strengths were used. Table 2 shows the growth of barley nutrients of different strength and corresponding variable hydrogen-ion concentrations. Because of the buffer action of the stronger nutrients, it was necessary to use more acid to keep the pH values constant.

TABLE 2

Growth of barley in three concentrations of Shive's R_4C_5 solution, February, 1920

NUMBER	TREATMENT	pH	0.025 ATMOSPHERE			0.1 ATMOSPHERE			0.4 ATMOSPHERE		
			Normality equivalent	Total weight of 4 plants	Relative growth	Normality equivalent	Total weight of 4 plants	Relative growth	Normality equivalent	Total weight of 4 plants	Relative growth
				gm.	*per cent*		*gm.*	*per cent*		*gm.*	*per cent*
1	Check...	5.8	0	0.8667	100.0	0	1.6615	100.0	0	2.7854	100.0
2	H_2SO_4...	3.4	N/2600	0.3997	46.1	N/2400	0.7814	47.0	N/1600	1.1999	43.1
3	H_2SO_4...	3.8	N/6200	0.5335	61.6	N/4800	0.8527	51.3	N/3300	1.1659	42.0
4	H_2SO_4...	4.0	N/9000	0.5332	61.5	N/7200	1.0371	62.4	N/4100	1.4744	52.9
5	H_2SO_4...	4.2	N/12000	0.6022	69.5	N/9600	1.0118	60.9	N/4700	1.8917	67.1

The normality equivalent given in the table is the normality of a solution made with pure water and the given amount of acid. Table 2 shows that the stronger the nutrient, the greater was the growth; but that there is a somewhat closely corresponding depression in growth of treated plants as conpared with check plants. The amounts given are the total weights of four barley plants. Figure 1 shows graphically the pH values of the different nutrient solutions after 3 weeks' growth of barley. These values were determined by the colorimetric method in duplicate solutions. The two checked quite closely in all readings and the values used are the average of both determinations. The change in values took place in proportion to the size of the plants. The richer the nutrient, the greater was the pH change; also, the weaker the acidity, the greater the change.

In May and June, 1920, new series of water cultures were conducted with rye, barley and corn. Shive's R_4C_5 nutrient of 0.2 atmospheres pressure was used. Lime water was added to bring it to a pH value of 6.3. Sulfuric acid

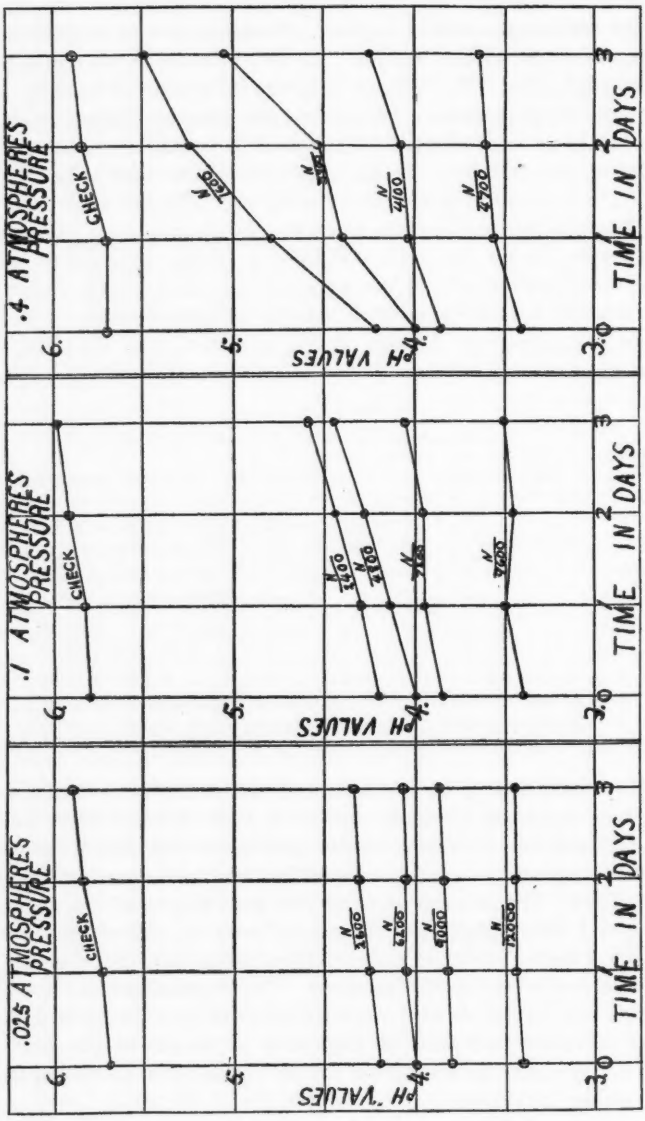

FIG. 1. CHANGE IN HYDROGEN-ION CONCENTRATION OF SHIVE'S R_4C_5 NUTRIENT SOLUTION OF VARYING STRENGTH AND ACIDITY, DUE TO GROWTH OF BARLEY IN IT

and aluminum sulfate were added to vary the pH from 3.6 to 5.7 on the acid and from 3.9 to 5.7 for the aluminum sulfate. The value pH 3.9 was taken as the strongest concentration for aluminum sulfate because it would take an excessively large quantity of aluminum sulfate to increase the concentration beyond pH 3.9. Table 3 shows the treatment, hydrogen-ion concentration of nutrient used, and the relative weights of rye, barley and yellow dent corn grown n water cultures. These results confirmed those of the previous tests, that aluminum salts on an average were less toxic than the same hydrogen-ion concentration of acid, even when the pH value was maintained by frequent changing of nutrient in large containers. The weights given are for the air-dry total roots and tops of four plants grown in duplicate jars. Shive's nutrient has a fairly large amount of phosphate in it, thus allowing for the possibility of aluminum precipitation. Plate 2 shows the growth of barley grown

TABLE 3

Growth of rye, barley and corn with constant hydrogen-ion concentration in Shive's R_4C_8 solution

NUMBER	TREATMENT	NORMALITY EQUIVALENT	pH	4 DRY RYE PLANTS, 3 WEEKS		4 DRY BARLEY PLANTS, 3 WEEKS		4 DRY CORN PLANTS, 10 DAYS	
				Total weight	Per cent of check	Total weight	Per cent of check	Total weight	Per cent of check
				gm.		*gm.*		*gm.*	
1	H_2SO_4.....	N/1800	3.6	0.5591	43	0.8647	31	1.45	78
2	H_2SO_4.....	N/3000	4.3	0.4033	31	1.6750	59	1.66	90
3	H_2SO_4.....	N/4000	5.0	0.9269	72	1.5277	54	2.29	124
4	H_2SO_4.....	N/4800	5.7	1.3241	103	2.6647	94	2.06	111
5	$Al_2(SO_4)_3$.....	N/1000	3.9	0.5416	43	0.9597	34	1.59	86
6	$Al_2(SO_4)_3$.....	N/1750	4.3	0.9155	71	1.8081	64	1.63	88
7	$Al_2(SO_4)_3$.....	N/2500	5.0	0.9671	75	2.6494	93	1.85	100
8	$Al_2(SO_4)_3$.....	N/3500	5.7	1.0857	84	2.7252	96	2.18	118
9	Check.....	0	6.3	1.2872	100	2.8363	100	1.85	100

in Shive's nutrient at the end of 3 weeks. Both roots and tops show a gradual increase in size when the hydrogen-ion concentration is lowered either in the presence of sulfuric acid or aluminum sulfate. Some difference in habit of root growth may be noted when comparing the acid with the aluminum salt.

Plate 3 shows the growth of dent corn with the treatments given in table 3. Although the nutrient was changed daily and the pH value kept constant, the corn shows an astonishingly healthy appearance at pH 3.6 in the sulfuric acid solution. It is doubtful if any natural soils ever have a pH value as low as 3.6. The results given in table 3 as well as those in table 1 show that corn has done better with a pH value around 5 than it has at 6.3 and 6.4.

In trying to correlate these results with those of Miyake (6) and Hartwell and Pember (3) it should be noted that Miyake did his work with distilled water containing no nutrients. Hartwell and Pember used a nutrient low

in phosphate, also one which they said "must not become physiologically alkaline as a result of the growth of the seedlings, for fear that the aluminum would be precipitated." To do this, they replaced part of the nitrate with an ammonium salt. A preliminary test with Hartwell and Pember's nutrient showed that there was a tendency for their nutrient not only not to become alkaline, but it actually became more acid as the plants removed ammonium ions.

Table 4 shows the relative elementary composition of the nutrient solutions used in the various tests. The ideal nutrient for such studies remains to be worked out. Hartwell and Pember's nutrient allows for very good growth in control bottles but the ammonium ion should be reduced in proportion to the nitrate ion in order more nearly to hold the nutrient at a fixed hydrogen-ion concentration. If nutrients are changed daily or oftener and the plants grown in large containers this is not so important a factor. While Tottingham's nutrient which we used, contained approximately the same amount of phosphorus as Hartwell and Pember's nutrient, it was very much more dilute

TABLE 4

Relative composition of different nutrients

ELEMENT	TOTTINGHAM'S	SHIVE'S	HARTWELL AND PEMBER'S
	gm. per liter	*gm. per liter*	*gm. per liter*
P	0.002	0.055	0.002
N	0.008	0.042	0.070
K	0.010	0.067	0.030
Ca	0.007	0.060	0.053
Mg	0.009	0.013	0.020
S	0.012	0.018	0.026

so far as the other elements were concerned, and did not allow good growth in the check solutions.

As a further check on the question, barley and rye were grown in Hartwell and Pember's nutrient. Table 5 gives the treatment, pH values and relative whole plant weights of the barley and rye at the end of 2 weeks. The pH values were held fairly constant by daily changes of nutrient in 2100-cc. bottles. In a separate test in the small 480-cc. bottles the same nutrient with barley growing in it changed from pH 6.0 to pH 4.3 in three days. The nutrient solutions above pH 4.2 all tend to approach an equilibrium at about pH 4.2 whether containing sulfuric acid or aluminum sulfate or no added treatment. Table 5 shows that aluminum sulfate is much more toxic to barley than sulfuric acid, except at a hydrogen-ion concentration of 5.0 or above. Similar results were obtained in small bottles. Rye is more tolerant than barley toward aluminum but even rye did better with the acid than it did with the aluminum sulfate. There was no sign of aluminum precipitation with Hartwell and Pember's nutrient as there was with Shive's, yet the

nutrient seemed to contain enough phosphate for normal growth. Plate 4 shows the relative growth of barley and rye at different hydrogen-ion concentrations with sulfuric acid and aluminum sulfate in Hartwell and Pember's nutrient. Both roots and tops of barley were stunted by the aluminum salts. These last results seem to show fairly conclusively that aluminum is in itself toxic. Everything seems to indicate that phosphorus will help prevent aluminum toxicity.

Both pot and field tests at the Indiana Agricultural Experiment Station (2) bear out the contention that aluminum is in itself toxic and that with many soils and crops the presence of soluble salts of aluminum is a more important factor than is the mere hydrogen-ion concentration of the soil.

It must be granted, however, that everything else being equal, the higher the hydrogen-ion concentration, the more chance there is for aluminum to

TABLE 5

Growth of barley and rye in Hartwell and Pember's nutrient

NUMBER	TREATMENT		pH	RELATIVE WEIGHTS	
				Barley	Rye
		cc.		*per cent*	*per cent*
1	0.2*N* H_2SO_4	2.00	3.9	73	65
2	0.2*N* H_2SO_4	1.00	4.2	93	95
3	0.2*N* H_2SO_4	0.50	5.0	90	90
4	0.2*N* H_2SO_4	0.25	5.7	101	95
5	0.2*N* $Al_2(SO_4)_3$	5.00	3.9	47	55
6	0.2*N* $Al_2(SO_4)_3$	1.30	4.2	68	65
7	0.2*N* $Al_2(SO_4)_3$	0.75	5.0	91	80
8	0.2*N* $Al_2(SO_4)_3$	0.50	5.7	121	90
9	(Check)		6.3	100	100

be present in soluble form. Thus for two reasons a determination of hydrogen-ion concentration in the soil is of value in determining its productivity.

The methods involving the use of salts of strong acids, such as the Hopkins potassium nitrate method, are very valuable from a practical as well as a theoretical standpoint. They show the amount of soluble aluminum present in the soil better than other types of soil acidity methods, such as the lime-water methods, which in adition measure the less toxic acid, organic compounds in the soil.

SUMMARY

1. Water cultures of barley, rye and pop corn in Tottingham's sub-optimum nutrient solution showed approximately the same degree of toxicity with acids and aluminum salts, of equal normality.

Wherever good growth was made the hydrogen-ion concentration of the solution was decreased.

About the same toxicity was obtained with acids and aluminum salts of nitric, sulfuric and hydrochloric acids. Phosphoric acid showed less, and tartaric acid the least, toxicity.

2. With Shive's R_4C_5 nutrient at 0.025, 0.1 and 0.4 atmospheres osmotic pressure, and with varying hydrogen-ion concentration, greater growth was obtained with the stronger solutions. The ratio of growth of treated plants at the varying pH values to that of the check was approximately the same with the nutrient at all strengths.

Wherever growth was made a lowering of the hydrogen-ion concentration was noted. This was in proportion to the size of the plants.

3. Three series of cultures were made with barley, rye and dent corn in Shive's nutrient, with four corresponding degrees of hydrogen-ion concentration for sulfuric acid and for aluminum sulfate. It was found that sulfuric acid was more toxic at the same pH value than aluminum sulfate with this nutrient. More or less precipitate was noticed in the bottles containing aluminum salts.

In this test 2100-cc. containers were used and the nutrient changed daily to prevent variation in pH value.

4. Hartwell and Pember's nutrient, which contains very much less phosphorate in proportion to the other elements, was used in cultures with barley and rye at the same pH value of sulfuric acid and aluminum sulfate.

In this nutrient aluminum sulphate proved to be much more toxic to barley than did the same hydrogen-ion of sulfuric acid. Rye was slightly more injured by the aluminum salts than by the acid.

Hartwell and Pember's nutrient tends to become more acid as the plants grow.

5. It is concluded that the toxicity of aluminum salts is due to the aluminum ion more than it is to the hydrogen ion on such plants as barley and that this toxicity is reduced when much phosphate is used in the nutrient.

These results confirm the conclusions of Hartwell and Pember and Miyake.

6. Acid soils are toxic to many plants largely because they contain easily soluble aluminum salts.

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PLATE 1

ILLUSTRATIONS OF WATER CULTURES WITH VARYING STRENGTHS OF SULFURIC ACID AND ALUMINUM SULFATE; TOTTINGHAM'S NUTRIENT.

Fig. 1. Rye.
Fig. 2. Barley.
Fig. 3. Pop Corn.

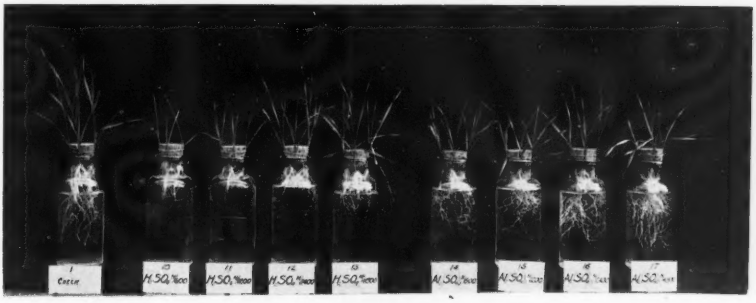


FIG. 1

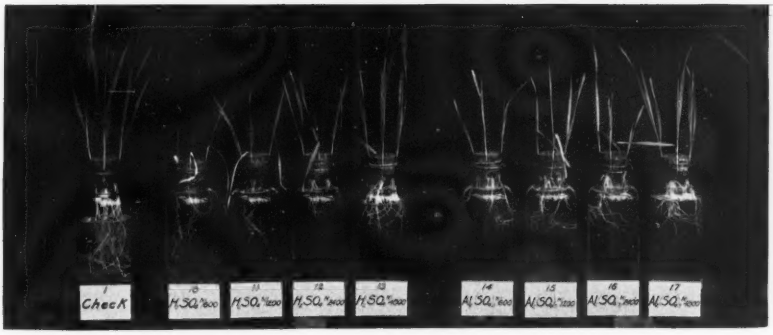


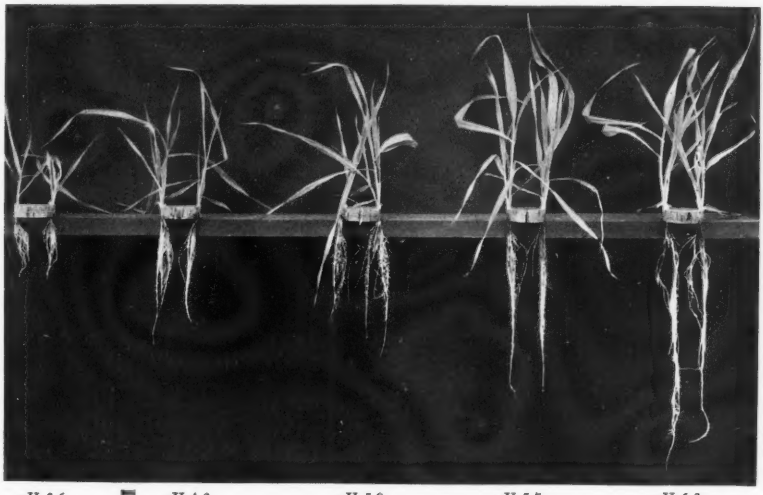
FIG. 2

FIG. 3

PLATE 2

ILLUSTRATIONS OF WATER CULTURES WITH BARLEY IN SHIVE'S NUTRIENT. SEE TABLE 3 FOR TREATMENTS.

Fig. 1. Growth of barley with varying pH values of sulfuric acid. Check plants at right.
Fig. 2. Growth of barley with varying pH values of aluminum sulfate. Check plants at right.



pH 3.6 H_2SO_4 | pH 4.3 H_2SO_4 | pH 5.0 H_2SO_4 | pH 5.7 H_2SO_4 | pH 6.3 Check

FIG. 1

pH 3.8 $Al_2(SO_4)_3$ | pH 4.3 $Al_2(SO_4)_3$ | pH 5.0 $Al_2(SO_4)_3$ | pH 5.7 $Al_2(SO_4)_3$ | pH 6.3 Check

FIG. 2

PLATE 3

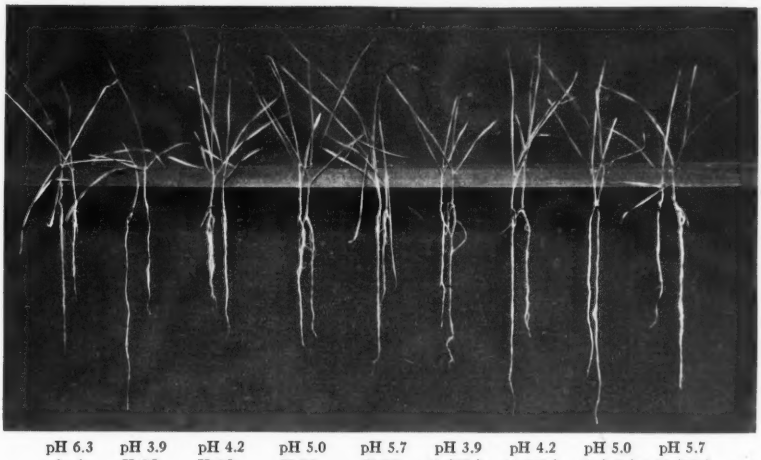
ILLUSTRATION OF WATER CULTURES WITH DENT CORN IN SHIVE'S NUTRIENT AT VARYING pH WITH H_2SO_4 AND $Al_2(SO_4)_3$. SEE TABLE 3 FOR TREATMENTS, CHECK AT RIGHT.

pH 3.6 H_2SO_4 | pH 4.3 H_2SO_4 | pH 5.0 H_2SO_4 | pH 5.7 H_2SO_4 | pH 3.8 $Al_2(SO_4)_3$ | pH 4.3 $Al_2(SO_4)_3$ | pH 5.0 $Al_2(SO_4)_3$ | pH 5.7 $Al_2(SO_4)_3$ | pH 6.3 Check

PLATE 4

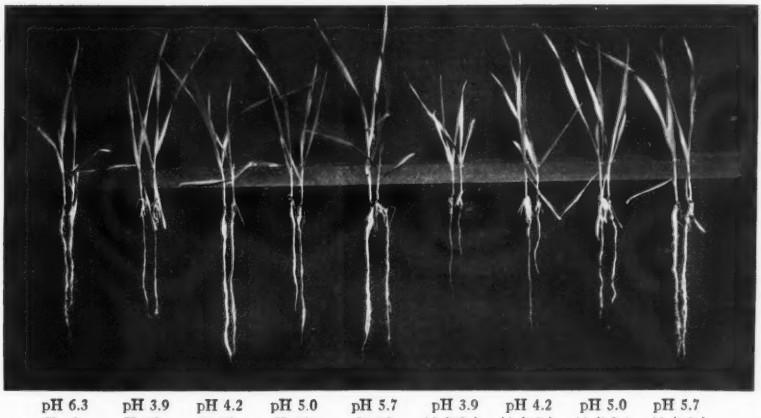
ILLUSTRATIONS OF WATER CULTURES IN HARTWELL AND PEMBER'S NUTRIENT. SEE TABLE 5 FOR TREATMENTS, CHECK AT LEFT; OTHERWISE NUMBERED FROM LEFT TO RIGHT.

Fig. 1. Rye.
Fig. 2. Barley.



pH 6.3 check | pH 3.9 H_2SO_4 | pH 4.2 H_2SO_4 | pH 5.0 H_2SO_4 | pH 5.7 H_2SO_4 | pH 3.9 $Al_2(SO_4)_3$ | pH 4.2 $Al_2(SO_4)_3$ | pH 5.0 $Al_2(SO_4)_3$ | pH 5.7 $Al_2(SO_4)_3$

FIG. 1



pH 6.3 Check | pH 3.9 H_2SO_4 | pH 4.2 H_2SO_4 | pH 5.0 H_2SO_4 | pH 5.7 H_2SO_4 | pH 3.9 $Al_2(SO_4)_3$ | pH 4.2 $Al_2(SO_4)_3$ | pH 5.0 $Al_2(SO_4)_3$ | pH 5.7 $Al_2(SO_4)_3$

FIG. 2

HU

THE CLASSIFICATION OF SOIL MOISTURE[1]

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INTRODUCTION

The soil moisture is generally classified into three forms; namely, hygroscopic, capillary, and gravitational water. This classification is based upon the vapor pressure exerted by the soil water and upon the water-holding capacity of the soil. This is the classification given in most texts on the subject and it is very satisfactory for many purposes.

A new classification of the soil moisture, based upon results obtained with the freezing-point and dilatometer methods, has been offered by Bouyoucos (3). The freezing-point lowering of a soil was found by Bouyoucos and McCool (4) to increase in approximately geometric progression as the moisture content decreased in arithmetric progression. This indicated that, contrary to the general belief, the concentration of the soil solution is not inversely proportional to the moisture content of the soil. The hypothesis, which was advanced to explain the results, assumes that the soil renders part of the soil water inactive as a solvent, thereby causing the soil solution to be more concentrated than is indicated by the percentage of moisture in the soil. The amount of this inactive or unfree water could not be measured satisfactorily by the freezing-point method so the dilatometer method was selected for this purpose. This method depends upon the principle that water expands on freezing and the amount of water frozen is indicated by the amount of expansion. Bouyoucos (3), using this method has classified the soil water as follows:

Gravitational
Free
Unfree { Capillary-adsorbed
Combined { water of solid solution or
water of hydration

[1] Part 2 of a thesis submitted at the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Published with the permission of the Director of the Wisconsin Agricultural Experiment Station.

The writer wishes to express his appreciation for the helpful suggestions and criticisms tendered by Prof. E. Truog.

The free water is that which will freeze the first time it is cooled to −1.5°C. The capillary-adsorbed water is the additional amount that can be frozen at lower temperatures. The combined water is that which cannot be frozen. The lowest temperature used was −78°C.

The properties attributed to the different forms of water in this new classification are very distinct. The free water[2] is considered as the only form acting as a solvent for the salts in the soil. A part of the capillary-adsorbed water is rendered free by successive freezing and thawing and then acts as a solvent. The combined water is supposed to exist as water of solid solution or as water of hydration and therefore is not a solvent. It is also considered that the free water is readily available to plants, that the capillary-adsorbed water is only slightly available, and that the combined water cannot be utilized by plants. Bouyoucos (3) also states that the free water would possess one velocity of evaporation, the capillary-adsorbed another, and the combined water still another. Thus it is seen that this investigator has given an entirely new conception of the moisture relations of the soil and the forms of water in the soil.

The dilatometer method has been used in studying the forms of water in hydrogels, and this has resulted, as in soils, in a conception different from that generally held, as to the forms of water present. Since the vapor-pressure and dilatometer methods have led to different conceptions as to the forms of water in both soils and hydrogels, it seems possible that one of the methods may be influenced by factors which have not been recognized. It is the purpose, therefore, of the present paper to review some of the work of previous investigators on the forms of water in hydrogels and soils, and to present some new data which indicate that all of the soil water acts as a solvent. The terms soil water or soil moisture are understood by the writer to include only that water which is lost from a soil by drying in an oven at 105°C. for 12 hours. No doubt soils contain more water, some of which is chemically combined, that would be lost on ignition. The moisture in hydrogels is expressed as total moisture on the wet basis, determined by ignition to constant weight.

HISTORICAL

Van Bemmelen (17, 18) studied the forms of water in hydrogels by determining the vapor pressure of the gel during dehydration and hydration. Dehydration curves for silica gels were obtained which had two transition points and a portion of the curve was nearly horizontal. This indicated a possible hydrate of silica. However van Bemmelen showed that the transition points do not represent definite hydrates since the water content at which

[2] In this paper the terms free water, unfree water, capillary-adsorbed water, and combined water are used with the meanings attached to them by Bouyoucos (1, 2, 3).

they occur varies widely, depending on the manner of preparation, age of the gel, and the temperature of dehydration. These characteristic points are explained by the structure of the gel. His results seemingly prove that the water is not in the form of hydrates but is absorbed. The fact that the water may be readily replaced by other liquids such as alcohol, glycerin, acetic acid, nitric acid, and concentrated sulfuric acid confirms the conclusion that the water in the hydrogel is not chemically combined.

Zsigmondy and his associates (20–22) performed similar experiments. With an improved apparatus they determined the vapor pressure of gels during dehydration and obtained results very similar to van Bemmelen's. The vapor pressure of alcogels and bensolgels was also determined and the vapor pressure curves were found to be similar to that obtained with hydrogels. All of this work indicates that the water, alcohol, benzene, or other liquid in the gel is not chemically combined with the solid but is absorbed and held in the capillary spaces of the gel.

The dilatometer method as a means of studying the forms of water in hydrogels has been used by Foote and Saxton (7, 9). They classified the water in gels into two forms, capillary and combined. The capillary water is that which will not freeze at 0°C. but can be frozen at lower temperatures. They determined the apparent capillary water, i.e., water which can be frozen only at temperatures below −6°C. The lowest temperature used was −78°C. The combined water is that which cannot be frozen. They have shown that the amount of water which cannot be frozen depends somewhat on the treatment of the gel after formation. The percentage of combined, or unfrozen, water was reduced to the lowest value by digesting the gel on the steam bath with a large amount of water. With alumina they obtained values of from 36.03 to 38.08 for the percentage of combined water. With ferric hydroxide the percentage of combined water varied from 5.42 to 21.96 depending upon the length of time the gel was digested on the steam bath. The percentage for silica gels varied from 22.87 to 30.6. Thus it is evident that a considerable but variable amount of water will not freeze at the temperature of −78°C. The results obtained for combined water by this method will obviously depend on freezing all of the capillary water. It seems possible that part of this water cannot be frozen and therefore the dilatometer method would classify some of it as combined water.

Vanzetti (19) studied the behavior of silica gels at low temperatures, using liquid air in some of his work. He prepared silica gels from silicate solutions of varying concentrations, subjected the gels to low temperatures and determined the ratio of water to SiO_2 in the gel. The ratio was found to vary from 2.25 in the gel formed from a 1 per cent SiO_2 solution to 0.72 in the gel formed from a 7 per cent solution. He concluded that the water was not chemically combined and that the absorption theory of van Bemmelen and the theory of the structure of gels account for all of the results obtained.

The effect of pressure on the water content of silica gels was determined by Lenher (12). When subjected to a pressure of 230 kgm. to the square inch the gel retained 77 per cent of water. Higher pressures reduced the water content. With a pressure of 272,000 kgm. to the square inch the water content was reduced to 12.5 per cent. This is approximately one-half the value obtained by Foote and Saxton for the combined water in silica gels. This and the other work cited indicate that the dilatometer method does not give a measure of the combined water in hydrogels and therefore it would not be expected to measure the combined water in soils.

Patten and Gallagher (15) have given a review of the literature on absorption, evaporation, and vapor pressure studies made with soils so it will only be necessary to consider the more recent investigations in this paper. Cameron and Gallagher (6) studied the rate of evaporation of water from soils over 95 per cent sulfuric acid and found that the rate of evaporation is nearly constant until the optimum moisture content of the soil is reached. From this point the rate gradually decreases and gives, when plotted, an even curve which indicates that there is no change in the physical state of the soil water. Patten and Gallagher (15) determined the vapor pressure of several soils at different moisture contents by placing the dry soils in desiccators over sulfuric acid of varying concentrations and obtained a uniform vapor pressure curve. These investigators have also determined the rate of absorption of water vapor by soils in atmospheres of different humidity. In every instance very regular rate curves were obtained, indicating that there is no abrupt change in the form of water in the soil as the moisture content is reduced from a high to a very low percentage.

Keen (10) used an improved method for studying the rate of evaporation of water from soils. A very thin layer of soil was placed in a wire basket so evaporation could take place from the top and bottom of the soil layer. This evaporation cell was placed over sulfuric acid of the desired concentration and the whole kept at constant temperature. The apparatus was so arranged that weighings could be made at frequent intervals without removing the soil from the desiccator. A similar apparatus has been used by the writer with satisfactory results. The results obtained by Keen show that the rate of evaporation decreases with the moisture content, and the conclusion is made that since there are no sharp breaks in the evaporation curve, there is no change in the physical state of the water as the moisture content is reduced. This conclusion was reasserted by Keen (11) after making a critical study of the data of Bouyoucos and McCool on the freezing-point lowering of soils.

Shull (16) measured the surface forces in soils by determining the moisture content at which Xanthium seed could no longer take up water from the soil, and the points of equilibrium between the seed and soil at different moisture contents. These results were compared with similar data in which the seed

was placed in salt solutions of known osmotic pressures. The seed reduced the moisture content of the soil to an air-dry condition and at this point the soil held the water with a force equal to about 1000 atmospheres. It is important to note that the seed was able to reduce the moisture content of the soil much below that of the unfree and even of the combined water content as would be indicated by the dilatometer method.

In studies on the displacement and freezing-point methods for determining the concentration of the soil solution, the writer (14) obtained results which indicate that the displaced solution is representative of all the water in the soil. The results also indicate that the soil does not cause a considerable amount of water to be removed from the role of a solvent. The writer (13) has also shown that solid material causes a freezing-point depression of a liquid in the film or capillary condition, and that after a certain moisture content is reached a small reduction in the amount of liquid present causes a great increase in the freezing-point depression of the liquid. These results indicate that as the moisture content is reduced a point is reached at which the water in the soil cannot be frozen on account of the great attraction between the soil and the water which is left and not because the water is no longer in the liquid state. It seems probable that the dilatometer method is a means of determining this point rather than the amount of combined water present.

Studies have been continued to determine whether or not all of the water in a soil acts as a solvent. If it does, further evidence is offered that the water is not combined but is held in the liquid state by the soil particles. The rate of evaporation of water from soils has also been determined and the results obtained agree with those of Keen so it does not seem necessary to include them here.

EXPERIMENTAL

If it is assumed that water is rendered unfree by a soil, then when a solution is added to a dry soil it would become more concentrated since part of the water would be withdrawn from the role of a solvent. It is possible to test this experimentally by both the displacement and freezing-point methods. In order to test this hypothesis by the displacement method, portions of four oven-dried soils were moistened with water, other portions were moistened with an alcohol solution, and still other portions with a glycerin solution. Each soil was brought to about its optimum moisture content with water and the two solutions. Alcohol and glycerin solutions were used because there is little probability of their reacting more than slightly with the material in the soil. The alcohol solution contained about 6 cc. of alcohol in 2000 cc. of water and the glycerin solution contained about 30 cc. of glycerin in 2000

cc. of water. The former solution gave a freezing-point depression of 0.090° and the latter a depression of 0.295°. After moistening, the soil solution was displaced from each portion and the freezing-point depression of the displaced solution determined. If water is not rendered unfree the freezing-point depression of the displaced alcohol solution should be 0.090° greater than that of the displaced water solution. Likewise the freezing-point depression of the displaced glycerin solution should be 0.295° greater. The experimental increase in the freezing-point depressions due to alcohol and glycerin are given in columns 5 and 7 of table 1.

There are two factors, adsorption and the difference in the nature of the solvent, which may affect the results obtained by both the displacement method and the freezing-point method. However the results obtained indicate that there is very little adsorption of either alcohol or glycerin. The

TABLE 1

The freezing-point depression (f. p. d.) of solutions displaced from soils, moistened as indicated, and the calculated depressions due to alcohol and glycerin; theoretical depression due to alcohol is 0.090° and to glycerin is 0.295°

SOIL	MOISTURE	MOISTENED WITH WATER	MOISTENED WITH ALCOHOL SOLUTION		MOISTENED WITH GLYCERIN SOLUTION	
		F. P. D. of displaced solution	F. P. D. of displaced solution	F. P. D. due to alcohol	F. P. D. of displaced solution	F. P. D. due to glycerin
	per cent	°C.	°C.	°C.	C.	°C.
Silt loam	25.0	0.055	0.138	0.083	0.348	0.293
Sand	15.0	0.050	0.125	0.075	0.335	0.285
Peat	225.0	0.116	0.198	0.082	0.405	0.289
Clay loam	30.0	0.051	0.140	0.089	0.355	0.304

total salts in the displaced solutions were determined in some cases and it was found that the amount of salts dissolved by the two solutions was very nearly the same as the amount dissolved by water. The agreement between the experimental and theoretical values is, in most cases, within the limit of experimental error.

The results indicate that water is not rendered unfree by a soil, as is shown by the following consideration. The silt loam soil contains 10.2 per cent of unfree water as determined by the dilatometer method. Therefore, at a moisture content of 25 per cent, 40 per cent of the water would be unfree. Assuming that this amount of water was withdrawn from the role of a solvent the freezing-point depression of the displaced alcohol solution would have been 0.193° instead of 0.138° and the depression due to the alcohol would have been 0.138° instead of 0.083°. Similar calculations for the glycerin show that the depression of the solution would have been 0.488° instead of 0.348° and the

depression due to glycerin would have been 0.433° instead of 0.293°. Therefore the experiment offers very good proof that all the soil water acts as a solvent.

The hypothesis was tested in a similar manner by the freezing-point method. Samples of the silt loam soil were brought to definite moisture contents with water. Other samples were brought to the same content with the same alcohol and glycerin solutions that were used in the preceding experiment. The freezing-point depression of all samples was determined in the usual manner. The depression obtained when the soil is moistened with water is due to the solid material and the salts in the soil solution. If water is not rendered unfree the freezing-point depression of the alcohol and glycerin solutions in the soil should be 0.090° and 0.295° greater respectively than the depression of the water in the soil. The values obtained for the depressions due to alcohol and glycerin are given in columns 4 and 6 of table 2.

TABLE 2

The freezing-point depression (f. p. d.) of water, an alcohol solution, and a glycerin solution in a silt loam soil at different moisture contents, and the calculated depressions due to the alcohol and glycerin; the theoretical depression due to alcohol is 0.090° and to glycerin is 0.295°

MOISTURE CONTENT OF SOIL	F. P. D. WATER	F. P. D. ALCOHOL SOLUTION	F. P. D. DUE TO ALCOHOL	F. P. D. GLYCERIN SOLUTION	F. P. D. DUE TO GLYCERIN
per cent	°C.	°C.	°C.	°C.	°C.
10.0	1.310	1.420	0.110	1.580	0.270
15.0	0.275	0.375	0.100	0.585	0.310
20.0	0.132	0.228	0.096	0.446	0.313
25.0	0.079	0.169	0.090	0.395	0.316
35.0	0.051	0.139	0.088	0.350	0.299
50.0	0.028	0.119	0.091	0.317	0.289

These results afford further proof that the soil does not withdraw part of the role of a solvent. If such were the case the alcohol and glycerin solutions would have been greatly concentrated at the lower moisture contents and in these cases the freezing-point depression due to alcohol and glycerin would have been many times the experimental values. Similar results have been reported (14) for a case in which a sugar solution was used with aluminium oxide.

DISCUSSION

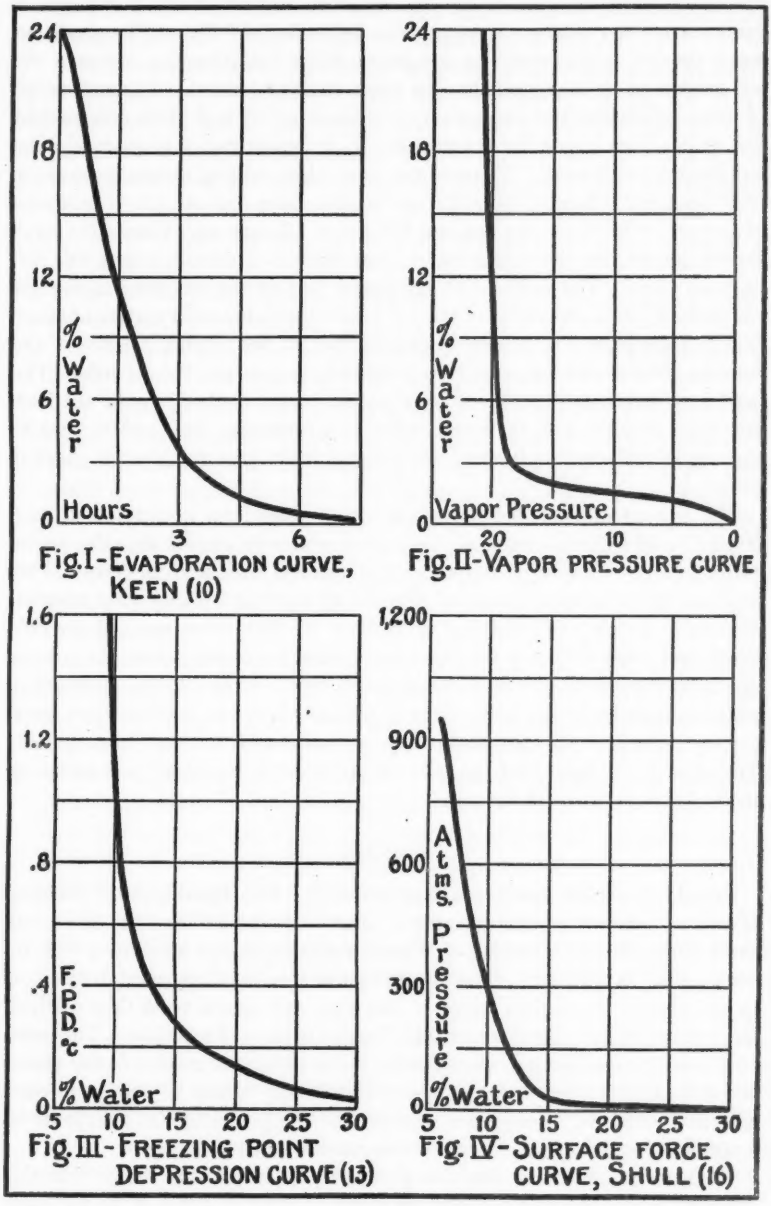
The results that have been obtained show that the soil does not render water inactive as a solvent. The water therefore must remain in the liquid state and does not become combined with any of the materials in the soil. There must, however, be a very great force holding the water to the soil. This force is sufficient to cause the vapor pressure of the soil water to be

greatly lowered at the lower moisture contents, to prevent considerable quantities of the water from freezing, to render part of the water unavailable to plants, and cause a considerable freezing-point depression of the soil water even at relatively high moisture contents. There are several methods by which this force may be measured or its relative value at different moisture contents indicated. Four methods which have been used are, (a) rate of evaporation, (b) freezing-point depression at different moisture contents, (c) vapor pressure during dehydration, and (d) equilibrium relations of the soil with seed of known water absorbing power. These methods of studying the force with which the water is held by the soil should give similar results.

In order to compare the results which have been obtained by the four methods, figures 1, 2, 3, and 4 are given. Figure 1 is the rate of evaporation of water from Hoos field soil (dunged plot) desiccated over 95 per cent sulfuric acid, as determined by Keen (10). Figure 2 is the vapor pressure curve of Superior clay, determined by the writer as follows. Samples of moist soil equal to 5 gm. of oven-dry soil were placed in 10 desiccators containing sulfuric acid of different concentrations thus giving different vapor pressures. The desiccators were kept at a constant temperature of 26°C. for 25 days after which time the moisture content of the soil was determined. Figure 3 is the freezing-point depression curve, previously given (13), for Carrington silt loam. Figure 4 is the curve obtained by Shull (16) for the subsoil of Oswego silt loam. Shull's measurements were made by determining the points of equilibrium between the soil and Xanthium seed of known water-absorbing power. Each method was used with a different soil but in all cases it was a fairly heavy type.

The curve obtained by the four methods are very similar. This would be expected since they are all graphic representations of the force with which water is held by the soil at different moisture contents. The main difference in the different curves is that the point of greatest curvature comes at different moisture contents. This is undoubtedly due for the most part to the difference in the sensitiveness of the methods. An increase in the force which could hardly be detected by vapor-pressure methods is readily shown by an increase in the freezing point depression. The freezing-point method and probably the method of Shull are more sensitive than the evaporation or vapor-pressure methods. Therefore the point of greatest curvature in the curve obtained by the former methods will be at higher moisture contents than the corresponding points obtained by the latter methods. All of these methods indicate that the water at low moisture contents is held with a much greater force than the additional water at the high moisture contents.

The dilatometer method of determining the forms of water in a soil probably only indicates the moisture contents at which this attractive force for the remaining water has certain values. The supposed unfree water content



FIGS. 1, 2, 3 AND 4. CURVES SHOWING THE SIMILARITY OF RESULTS OBTAINED BY FOUR METHODS OF STUDYING THE FORCE WITH WHICH SOILS HOLD WATER

of a soil is probably very nearly that moisture content at which the force is great enough to produce a freezing-point depression of 1.5°C. The combined water content is that moisture content at which the attraction between the soil and the water is so great that the water cannot be frozen. The percentage of water which does not freeze the first time at −1.5° is of particular interest for, as has been shown by Bouyoucos (1), it approximates very closely the wilting point of the soil, The moisture equivalent, wilting point, hygroscopic coefficient, water-holding capacity, and unfree water content are all measures of the attractive force the soil has for water. Briggs and Shantz (5) have shown, for all but the unfree water, that there is a rather definite relation between them. The writer (14) has shown that at the moisture equivalent the freezing-point depression of the soil water due to the solid material is very nearly a constant. It is very probable that at the wilting coefficient the freezing-point depression would be practically a constant for all soils. The combined water, as determined by the dilatometer method, would not bear any definite relation to these points for in determining the combined water the soil is subjected to freezing and thawing which greatly alters its physical properties.

The amount of water held by a soil with a given force is determined very largely by its colloidal material. Any treatment which alters the soil colloids will affect the amount of water held by the soil with a given force. This has been shown by Bouyoucos and McCool (4) with the freezing-point method. Successive freezing and thawing or ignition, by destroying some of the colloidal properties of heavy soils greatly reduces the freezing-point depression due to solid material at a given moisture content. Keen (10) has shown that water evaporates much faster from a soil in which the colloids have been destroyed by ignition than from the same soil which has not been ignited. Therefore it is evident that the soil colloids are very important in considering the moisture relations of the soil.

SUMMARY

In order to explain results obtained in a study of the freezing-point lowering of soils at different moisture contents, Bouyoucos and McCool (4) advanced the hypothesis that a portion of the soil water is inactive or unfree, that is, does not act as a solvent. The dilatometer method was later used to measure quantitatively the unfree water of the soil, and based upon that method Bouyoucos (3) has offered a new classification of the soil moisture. The most striking feature of the new classification is the unfree water, that is, the water which is not supposed to act as a solvent although it may be present in considerable amounts. Bouyoucos reports that the percentage of this form of water in soils varies from 1.2 in a coarse sand to 22.84 in a clay.

Evidence presented in this and previous papers (13, 14) shows that the dilatometer method does not measure different forms of water in the soil, and

that soils do not contain a considerable percentage of water which does not act as a solvent. This evidence is summarized as follows:

1. The much greater increase in the freezing-point depression of soils with a decrease in the moisture content than is indicated by the law of inverse proportion, is due to the solid material and not to the existence of unfree water which would cause a greater concentration of the soil solution. It has been shown that solid material causes a depression of the freezing-point of water, benzene, and nitrobenzene in the film or capillary condition.

2. Alcohol and glycerin solutions are not made more concentrated when added to a dry soil, as would be the case if part of the water was rendered unfree by the soil. Therefore all of the soil water must act as a solvent and exist in the liquid condition.

3. It is possible to displace part of the soil solution from a soil whose moisture content is less than that of the unfree water.

4. A number of investigators have shown that the water of certain inorganic hydrogels is not combined water. However, these hydrogels contain a considerable amount of water which cannot be frozen and a still larger amount which would be classified as unfree water under the new classification.

5. Studies on the rate of evaporation of water from soils, the vapor pressure at different moisture contents, the equilibrium relations with seeds, and the freezing-point depression due to solid material do not indicate the presence of different forms of soil water such as are given in the dilatometer classification.

All of the results obtained are readily explained as follows. At moisture contents below the water-holding capacity of the soil the water is held to the soil by an attractive force commonly called adhesion. As the moisture content of the soil gradually decreases the force with which the remaining water is held continually increases. This causes an increase in the freezing-point depression of the soil water, a decrease in the rate of evaporation, and a decrease in the vapor pressure of the soil water as the moisture content is reduced. This force is great enough to prevent part of the soil water from being frozen at very low temperatures.

The same general conclusion concerning the moisture relations of soils, as drawn by Keen (11) from his investigation of the rate of evaporation of water from the soil, and from a study of the freezing-point data of Bouyoucos and McCool, follows:

> The water present is subjected to the same law over the whole experimental range and the various constant and critical points shown by soil at varying degrees of water content, are approximate equilibrium values only and do not indicate any break or abrupt change in the physical condition of the soil moisture.

The old classification of the soil moisture into hygroscopic, capillary, and gravitational water has certain objectional features but seems to be the best

classification yet offered for most purposes. It is at least very useful in many respects.

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FERROUS SULFATE TREATMENT OF SOIL AS INFLUENCING THE SOIL SOLUTION OBTAINED BY THE LIPMAN PRESSURE METHOD

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In connection with studies conducted by the writer during the past five years on chlorosis of citrus trees, some interesting evidences of the utility of his pressure method (1) for obtaining the soil solution were adduced. While some of the results are fragmentary, I consider them interesting enough to present to those who are working on problems either of the soil solution or of chlorosis, or of both.

The soil involved in these experiments was that of a young lemon orchard in southern California in which the trees were affected by a type of chlorosis common under certain circumstances. Among other attempts to cure the diseased trees, $FeSO_4$ was applied to the soil in which they were growing. From 5 to 10 pounds of commercial $FeSO_4$ was used per tree. It was applied in a dilute solution over an area represented by a circle 15 feet in diameter with the tree trunk for center. Control trees were included in the experiment which received the same amount of water as the $FeSO_4$ treated trees, but no other treatment. After some weeks a composite soil sample of several borings was made respectively from a treated and from a control tree. The soil was sampled to a depth of 12 inches.

When the samples were received in the laboratory, they were thoroughly mixed, made up to approximately optimum moisture content and allowed to stand in tightly stoppered containers for one day. At the end of that time, they were submitted to pressure in the apparatus described in the paper cited above. The solutions thus obtained were analyzed for total solids, non-volatile solids, calcium, potassium and phosphorous. Table 1 gives the results obtained in the analyses.

TABLE 1

Analyses of 25 cc. of extract representing 125 grams of soil

TREATMENT	TOTAL SOLIDS	NON-VOLATILE SOLIDS	Ca	K	P
	grams	*grams*	*grams*	*grams*	*grams*
FSO_4.....	0.0585	0.0420	0.0044	0.0049	0.0027
Untreated.....	0.0431	0.0266	0.0023	0.0034	0.0018

The foregoing data show perfectly clearly the effectiveness of ferrous sulfate as a modifier of the composition of the soil solution. It appears to increase markedly the content of non-volatile solids in the soil solution and to precipitate the dissolved organic matter therein. The iron evidently substitutes itself readily for the common bases, calcium and potassium, and for some reason seems, besides, to bring more phosphorus into solution. Other unpublished data in my possession prove conclusively that $FeSO_4$ treatment of soil results in bringing added amounts of calcium and potassium into the soil solution. The study here described was carried out before we had become fully impressed with the profound significance of soil variability and its relations with soil sampling regarding which this laboratory was the first to make important contributions. For that reason, no control of variability was included in obtaining the data given above. Nevertheless, the effects are so uniformly consistent in one direction and so well supported by other data as above stated, that a note with regard to them seems eminently desirable.

I wish particularly to call attention to the evidence furnished in table 1 of the utility of my pressure method for obtaining the solution since I have not heretofore had an opportunity of giving actual data of analyses based thereon. Other and much fuller evidence along that line will soon be published by myself and by others.

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THE MOVEMENT OF SATURATED WATER VAPOR THROUGH QUARTZ FLOUR

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Water may move through the soil in either the liquid or vapor state. The liquid movement is of the greatest importance, especially when the soil has a comparatively high moisture content and when it is compacted to such an extent that the films between the soil grains may form a continuous liquid path through the soil. It is a common farm practice to work up the surface of the soil into a mulch to prevent this liquid movement, but the mulch will not prevent the gaseous water from diffusing up through the soil. The gaseous movement is extremely small in comparison with the liquid movement. Patten and Gallagher (1) have determined the rate of adsorption and evaporation of water in quartz flour in atmospheres of different degrees of humidity and were able to approach the equilibrium point starting with both dry and wet soil. They also showed that the adsorption of water vapor decreases with increase in temperature. This investigation is an attempt to get more definite knowledge of the nature of water vapor movement.

Consider a tube full of soil with one end closed and the other exposed to saturated water vapor. The quantity of water in the soil may be expressed by the following definite integral:

$$q = \int_a^b (\rho + c)\, dx$$

where q is the total quantity of water in the soil, ρ is the "density" of the liquid phase, c is the "density" of the gaseous phase, and x is the distance from an appropriate origin. Assume that $\rho\,(c_0 - c) =$ a constant K_1, where c_0 is the density of saturated water vapor. This assumption is based on an investigation which is being conducted at this station by Thomas. (3)

Substituting

$$q = \int_a^b \left(\frac{K_1}{c_0 - c} + c\right) dx$$

[1] The author feels much indebted to Dr. Willard Gardner for assistance in the mathematical development and to Prof. M. D. Thomas for many helpful suggestions in the laboratory technique.

Differentiating with respect to the time

$$\frac{dq}{dt} = \int_a^b \left[\frac{K_1}{(c_o - c)^2} + 1\right]\frac{dc}{dt}\,dx \tag{2}$$

Assume, as Patten and Waggaman (2) have done, that

$$\frac{dc}{dt} = K_3\,(c_o - c) \tag{3}$$

In any length of soil tube when a state of steady flow is reached, assume that the vapor density is a linear function of x, that is, $c_o = c - K_3x$. Substituting for c and $\frac{dc}{dt}$ in (2)

$$\frac{dq}{dt} = \int_a^b \left(\frac{K_1}{(K_2\,x)^2} + 1\right) K_2K_3\,x\,dx \tag{4}$$

Integrating,

$$\frac{dq}{dt} = \frac{K_2K_3}{2}\,x^2\,\Big]_a^b + \frac{K_1K_3}{K_2}\log x\,\Big]_a^b \tag{5}$$

The integral becomes indeterminate when integrated between 0 and h, for the second term becomes $-\infty$ when the lower limit is substituted. To avoid this, integrate between $+1$ and h.

This gives

$$\frac{dq}{dt} = \frac{K_2K_3}{2}\,h^2 + \frac{K_1K_3}{K_2}\log h - \frac{K_2K_3}{2} \tag{6}$$

Putting

$$\frac{K_2K_3}{2} = A \text{ and } \frac{K_1K_3}{K_2} = B, \frac{dq}{dt} = Ah^2 + B\log h - A \tag{7}$$

The following experimental method was used to test the accuracy of this equation. Finely ground quartz flour was placed in weighing bottles in different quantities so that when the bottles were tapped until the flour would settle no further, the depths in the various bottles were in the ratio of 1, 2, 3, etc., each depth being duplicated. The bottles were then placed in a desiccator containing water and the desiccator evacuated and placed in a thermostat that could easily be regulated within one-tenth of a degree.

Evacuating the desiccator would not affect the mechanism of the water vapor movement or the ultimate equilibrium point. It would only hasten the rate at

which the water vapor moves. The samples were weighed several times the first day and once per day thereafter. As soon as the lid of the desiccator was removed, the lids were quickly placed on the weighing bottles so that none of

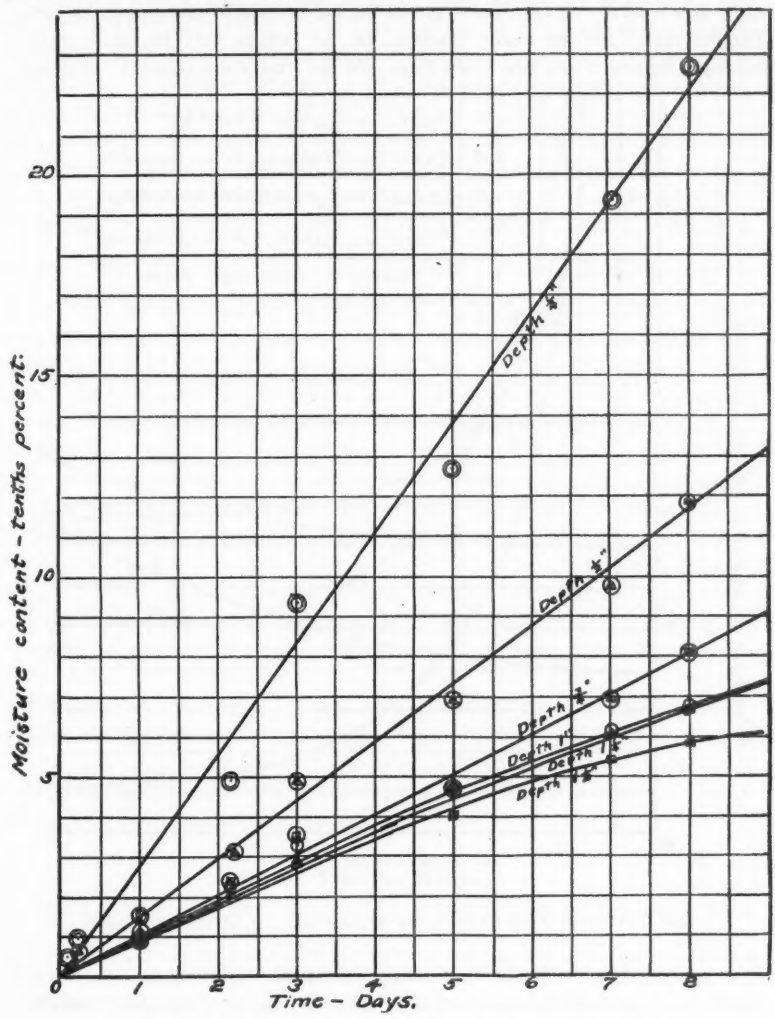

FIG. 1. RELATION BETWEEN THE MOISTURE CONTENT AND TIME

the moisture could escape. Exactly the same method of evacuating the desiccator was followed each time and the pressure inside was found to be approximately 0.7 cm. of mercury, or about one-hundreth of an atmosphere.

Quartz flour was chosen in order that all chemical and biological influences might be eliminated as far as possible.

The results obtained from weighing the bottles are shown in figure 1, the water adsorbed divided by the weight of the soil being plotted against the time. The correction for the water adsorbed on the bottles may be made in the following manner: At any given time plot the "moisture content" obtained

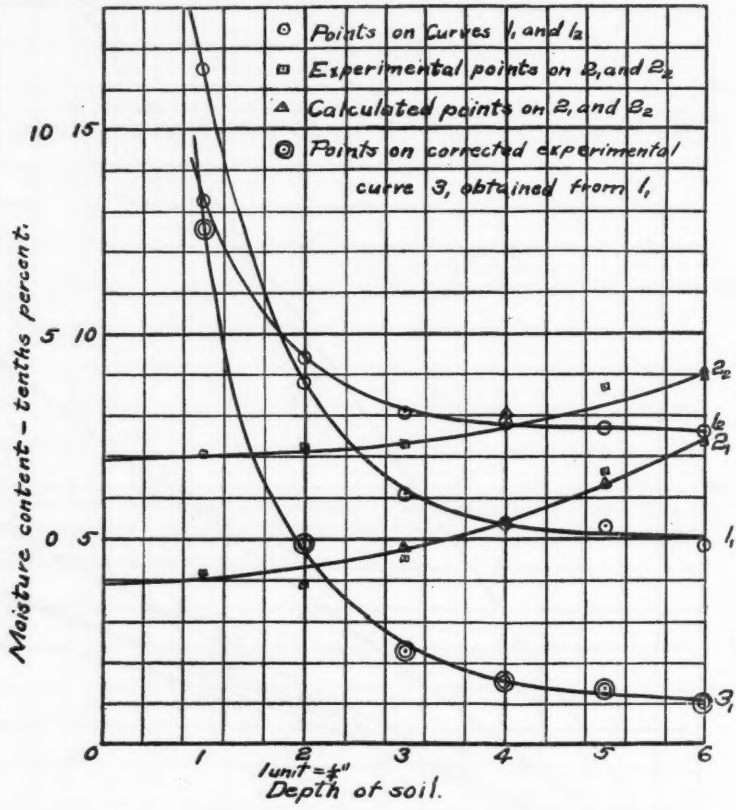

FIG. 2. RELATION BETWEEN MOISTURE CONTENT AND DEPTH OF SAMPLE

from figure 1 against the depth of soil. Taking the ordinates at time 3 and 6 the curves 1_1 and 1_2 in figure 2 are obtained. By multiplying each "moisture percentage" by the depth of the corresponding sample, curves 2_1 and 2_2 in figure 2 are obtained. The curves express the relationship between the quantity of water adsorbed and the depth of the sample at the time indicated. These same curves might be obtained directly by plotting quantity of water adsorbed against the depth at a given time from the original results. The

advantage of the method used lies in the fact that average values are obtained as compared with single values by a direct method. By extending the curves back to the Y axis, it can readily be seen that when the depth of the soil is 0 the quantity of water adsorbed is about 2 units where time is 3 and about 4 units where time is 6, which is the amount of water adsorbed on the glass. By reducing each ordinate of the curve 1_1 by this amount, the curve 3_1 is obtained which expresses the true relationship between the average moisture percentage and the depth. This curve is an hyperbola over the range indicated and its equation may readily be found. It can be seen from figure 1 that for any given depth the rate of increase of the moisture content through the range investigated is practically constant. Therefore, curves 2_1 and 2_2 in figure 2 are also curves expressing the relation between $\frac{dq}{dt}$ and the depth for a given time, which are the variables in equation (6). If the theoretical considerations upon which this equation is based are correct the equation will fit the curves 2_1 and 2_2. By using the first and last points on the experimental curves, the values of the constants A and B in equation (7) were determined and then the theoretical points on the curve calculated with these constants. The position of the calculated points can be seen in the figure. The values of the constants K_1, K_2, and K_3 cannot be determined from the experimental data. K_1 and K_3 are constants which depend only on the kind of soil used. K_2, which is the vapor density gradient, is a function of the time, and hence the values of A and B in equation (7) vary with the time, for they both contain K_2. If the value of any one of these constants is determined, the others may readily be calculated. The value of K_1 may be obtained by measuring the vapor pressure of the soil at several moisture contents as has been shown by Thomas.

This paper is an attempt to use the well-known principles of mechanics to solve the problem of water vapor movement through soils. Starting with several reasonable assumptions, an equation is developed which expresses the relation between the rate of adsorption and the depth of the soil. The results show that qualitatively the theory is in accord with the facts.

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